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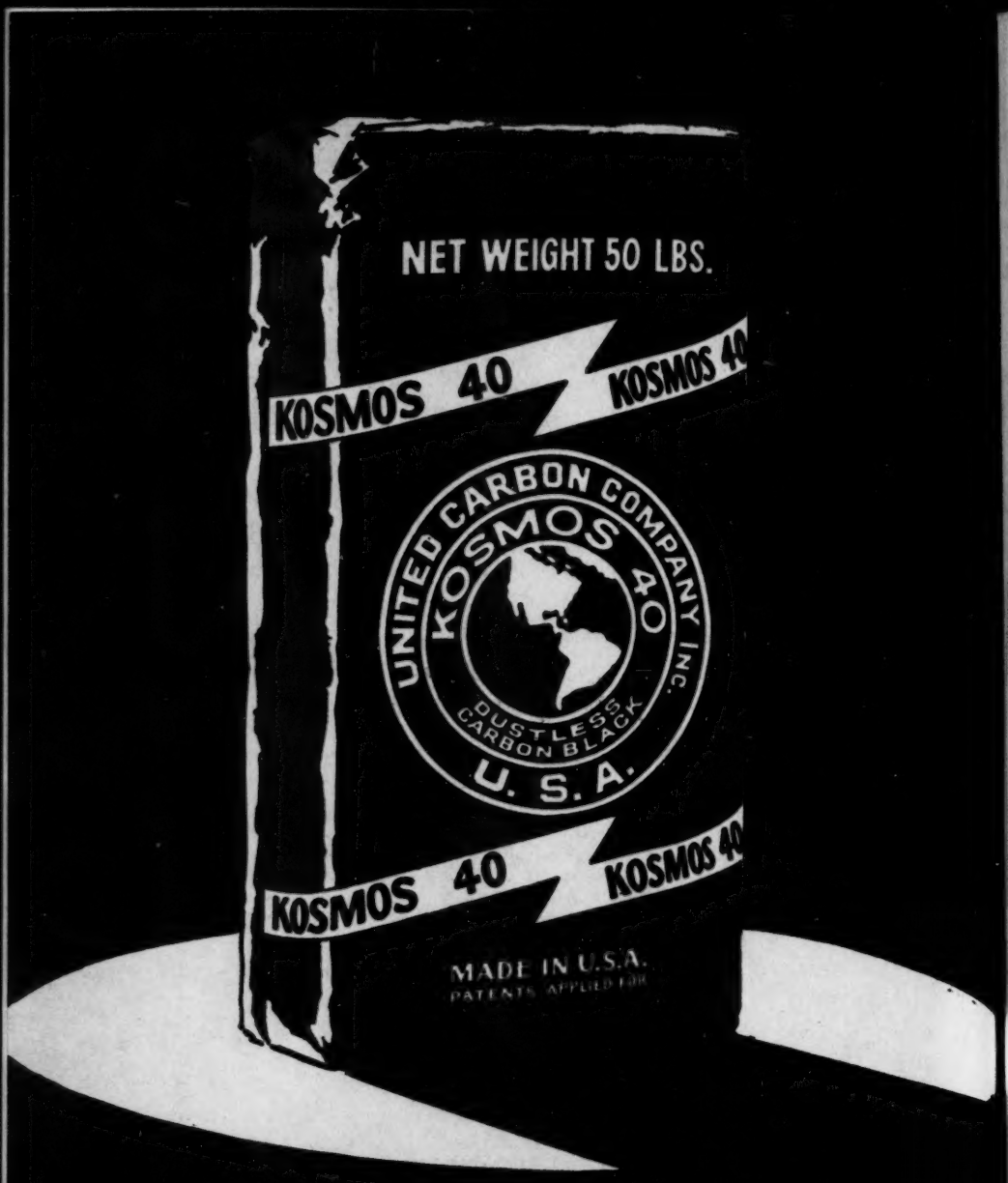

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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RUBBER METABOLISM IN PLANT LIFE. DEVELOPMENT OF A NEW THEORY *

R. F. A. ALTMAN

INDONESIAN INSTITUTE FOR RUBBER RESEARCH, BUITENZORG, JAVA

THE PROBLEM

What does the problem of rubber metabolism actually imply? In the opinion of the present author, a clear insight can best be obtained by considering the problem from four points of view.

1. SYNTHESIS

The fact has already been established that rubber is synthesized by the plant. The questions then arise as to which tissues are the source of rubber, and how and from what compounds (precursors) rubber is formed.

2. TRANSPORT

Rubber occurs in almost every part of the plant. Is rubber transported through the plant organism? If so, how can the fact be explained that this high polymer of pronounced hydrophobic character diffuses through the cell walls? If not, is rubber synthesized locally from easily transportable precursors?

3. POLYMERIZATION

Rubber obtained from the latex of *Hevea brasiliensis* is a high polymer. Does the process of polymerization take place independently of the process of synthesis or is synthesis immediately followed by polymerization?

4. BREAKDOWN

Some investigators have considered rubber to be a waste product[1]; others have advanced numerous arguments to show that rubber has a physiological function[2]. The former base their theory mainly on the inertness of the rubber hydrocarbon and on the fact that rubber is present in old fallen leaves; and this, in their opinion, is incompatible with a certain food-value of the high polymer. It will be proved in the present paper that these arguments are extremely weak; on the other hand, supporters of the other theory have thus far failed to show how and for what purpose rubber is used by the plant. So the question is still to be answered whether or not rubber is broken down by the plant[3].

All this shows in a convincing manner that the problem of rubber metabolism is far from settled, and why this most interesting problem still continues to attract the attention of so many scientists.

* An original contribution. The present address of the author is Unilever Research Laboratorium, Zwijndrecht, Holland.

Systematic analysis of the latex of *Hevea brasiliensis* gave results[4] which induced the writer to study the metabolism of rubber more closely. As it was realized that knowledge of the composition of latex, however extensive, was not sufficient to give a clear picture of all the processes which result in the formation and decomposition (utilization) of rubber in the plant, the need for a more extensive analytical chemical investigation was obvious. A complete analysis of the tissues immediately bordering the latex-vessels naturally came to mind first, since this is the only means of getting an insight into the nature of the latex components which enter the latex vessel from outside by diffusion. Reasoning in this way, the conclusion was soon reached that other tissues located further away should also be investigated; that, in fact, an analysis of the whole *Hevea* tree, from the topmost leaves down to the lowest tips of the roots, was necessary.

It was evident, however, that such an exhaustive investigation would easily take the time of a staff of chemists for many years; hence the author found himself obliged to carry out only a very limited part of this otherwise attractive program.

ANALYSIS OF THE HEVEA TREE

As already remarked, it would be practically impossible to analyze completely all parts of the *Hevea* tree. It is also evident that the rubber content alone, even if this were known for all parts of the tree, would not provide the slightest information as to the nature of either the rubber precursors or the decomposition products.

SAMPLES

Concerning the choice of samples to be analyzed, those parts of the tree which are botanically most important[5] naturally come into consideration first.

In analyzing *Hevea* latex, the author in most cases started from samples exclusively from the Tjirandji 1 clone, hence it was considered advisable to use a specimen from the same clone for the analysis of the different parts of the tree. For this purpose a 9-year-old tree from the Tjiomas Experimental Garden (Buitenzorg, Java) was sacrificed, and the following samples were taken from it.

A. *Root:* (1) wood, (2) cambium, (3) soft bark, (4) hard bark, (5) cork;

B. *Trunk:* (1) wood, (2) cambium, (3) soft bark, (4) hard bark, (5) cork;

C. *Branches:* (1) green twigs, (2) branches without pith, (3) pith only;

D. *Leaves:* (1) very young brown leaves, (2) half grown green leaves, (3) full grown green leaves, (4) full grown yellow leaves, still attached to the tree, (5) leaves, just fallen off, (6) petioles;

E. *Young fruit:* (1) endosperm, (2) endocarp, (3) exocarp;

F. *Mature fruit:* (1) endosperm, (2) seed coat, (3) endocarp, (4) exocarp;

G. *Flower:* the flowers were used without petioles.

To slow down, or stop completely, enzymatic reactions in the fresh plant material, the samples were heated at 120° C in an autoclave for a short time[6]. By this means oxidative decomposition of the rubber hydrocarbon was prevented[7], and at the same time the heating period was too short to bring about radical changes in the constitution of the other plant substances, which were determined as groups of compounds.

The samples thus obtained were dried in a vacuum desiccator over calcium oxide at about 60° C, and then finely powdered in a Pepping mill. Care was taken that the temperature[8] during milling did not exceed 60° C.

EXPERIMENTAL TECHNIQUE

The question as to which components of the samples should be determined is more difficult to answer. Should, in addition to the rubber, the proteins, lipids, or sugars be determined? Or are the amino acids, inositol derivatives, and incrusting substances more important? Every phytochemist is fully aware of the difficulties attached to the quantitative determination of each of these groups, for the method of analysis for such determinations is deficient in various respects. Certain considerations finally led the author to follow a method described by Waksman and Stevens[9], by the aid of which it is possible to form a well founded idea of the chemical constitution of all kinds of plant material.

The method of Waksman and Stevens, although followed in its general lines, needed important alterations in determining the rubber content, for the latter is not included in the original method. A short description of the procedure chosen by the present author follows.

A five-gram sample (in duplicate) is weighed, packed in filter paper, and extracted with alcohol in a Soxhlet apparatus (equipped with interchangeable ground-glass joints) in darkness, and, if possible, under reduced pressure. After 48 hours the boiling flask is replaced by one containing anhydrous benzene. Without evaporating the alcohol left in the extraction thimble, extraction with benzene is carried out for 48 hours in the same apparatus under the same conditions. Possibly the extraction times were slightly longer than strictly necessary; on the other hand, the presence of gel rubber, which does not dissolve easily, had to be taken into account[10]. In addition, the experimental results obtained by Whittenberger, Brice and Copley[11] and by Rollins, Bailey and de Gruy[12] show that a substantial proportion of the rubber in plant material is very difficult to extract by conventional methods.

Since extraction takes place in darkness, and atmospheric oxygen is almost completely replaced by solvent vapor, oxidation does not occur during extraction.

The alcohol and benzene extracts obtained are evaporated in a vacuum and dried in a vacuum desiccator over calcium oxide.

As the samples are freed from rubber, the earlier precautions (working in darkness and in vacuo) can now be disregarded; the extraction thimble is freed of benzene in a drying oven at 90–100° C, and is extracted in the normal way in a Soxhlet apparatus with water for 6 hours.

Hemicellulose, cellulose, proteins, and lignins in the extracted sample are then determined by the method given by Waksman and Stevens.

In addition to these determinations, the pentosan and methylpentosan contents of the original samples are determined according to the well known method of Tollens and of Ellet and Tollens[13].

Last but not least, the rubber content[14] is determined by digesting the dried benzene extract with alcoholic potash, and drying and weighing the residue according to Van der Bie[15].

RESULTS OF ANALYSIS

The analytical results are summarized in the following table; all values are expressed in percentage of absolutely dry samples.

DISCUSSION OF RESULTS

The importance of the analytical results will find full expression in the new theory to be proposed. For the moment a few remarks on the general significance of the values will suffice.

The content of alcohol-soluble and water-soluble substances was highest in those samples which were prepared from parts of the plant in which, physiologically speaking, the greatest activity is developed, *i.e.*, green leaf, cambium, fruit endosperm, etc. Particular attention should be paid to the extraordinarily high values for the exocarp of the young fruit (E_3) and for the endocarp of the young and ripe fruit (E_2 and $F)_3$, indicating that important transformations also take place in these parts of the plant. This is in complete accord with what actually happens, since in a comparatively short time very radical changes take place in the endocarp/exocarp system. These changes, which led to the development of the new theory, will be referred to repeatedly later.

Sample no.	Alcohol extract	Benzene extract	Rubber content	Water extract	Hemi-celluloses	Celluloses	Lignins	Methyl-pentosans	Pentosans	Proteins
A 1	4.22	0.11	0.00	3.17	20.68	31.65	20.36	3.92	16.41	0.60
2	28.80	4.96	4.96	35.87	11.68	8.85	6.37	3.39	7.67	1.65
3	15.11	6.57	6.57	23.10	12.92	11.39	12.70	3.52	10.63	1.64
4	7.78	2.00	2.00	13.45	13.03	16.40	20.92	4.40	13.27	1.47
5	6.90	1.05	0.06	4.50	11.51	12.97	28.14	3.36	12.75	1.67
B 1	5.18	0.11	0.01	7.19	21.06	31.96	18.62	4.76	15.98	0.16
2	37.81	13.09	13.09	26.08	8.66	6.72	9.34	4.78	9.79	1.82
3	18.52	14.39	14.18	11.85	15.87	9.74	11.43	4.44	10.58	1.48
4	6.49	1.36	0.80	7.02	18.32	21.05	23.35	4.39	17.80	0.94
5	6.77	0.52	0.03	4.17	15.82	13.87	28.15	4.69	15.64	1.98
C 1	9.75	3.72	3.72	9.65	21.22	16.19	16.79	4.22	12.27	1.61
2	8.22	2.35	2.35	10.14	20.60	19.10	16.76	4.48	13.45	1.07
3	16.45	0.55	0.22	16.77	19.52	16.66	15.46	4.60	12.50	0.55
D 1	31.15	1.40	1.31	18.37	6.77	3.97	4.08	3.63	4.15	2.47
2	30.21	1.17	1.12	13.94	8.19	6.28	10.64	4.10	5.15	2.45
3	29.76	1.93	1.50	9.42	9.53	8.56	15.52	4.60	7.39	3.32
4	20.47	2.24	1.81	9.81	11.73	12.69	23.13	4.16	9.27	1.92
5	17.02	3.53	1.88	8.46	13.49	14.67	23.77	3.97	10.40	2.03
6	14.77	3.86	3.75	10.47	17.53	20.18	17.75	4.63	15.77	1.54
E 1	25.47	1.67	0.52	21.17	14.99	11.95	11.85	2.50	13.78	3.67
2	30.18	0.32	0.32	6.44	25.24	19.98	6.02	3.09	27.41	0.97
3	23.68	6.87	6.77	21.46	11.95	11.21	9.41	3.22	8.73	3.07
F 1	58.66	1.38	0.02	13.50	7.44	1.28	4.36	5.10	0.00	0.43
2	3.40	0.11	0.01	0.96	25.58	23.35	32.73	5.12	28.36	0.43
3	17.13	0.04	0.00	2.14	27.84	27.94	13.28	5.14	31.80	0.21
4	5.60	10.65	10.65	36.11	9.55	11.64	14.27	4.39	8.12	0.22
G	20.76	3.07	2.97	21.19	9.64	7.10	12.08	3.23	7.74	2.97

It should also be mentioned that the alcohol and water extracts of the cambia on the one hand, and of the soft bark on the other, show considerable differences. This was sufficient guarantee of accurate splitting of these parts of the bark. As a matter of fact, the cambium consists of a thin layer of only a few cells[6], so an incomplete mechanical separation between cambium and soft bark might well be feared.

The values for the benzene extract in comparison with those for the rubber content are especially important in connection with the breakdown of rubber in the living plant.

It is most remarkable that the benzene extracts in some cases show no variations from the rubber contents (see table) and in others very great ones (up to more than 50 per cent). To be sure, this signifies that the benzene extract of some samples consists entirely of rubber, whereas that of other samples consists only partly of rubber; the other part, being soluble in alcoholic potash, obviously contains acidic substances. The latter can be easily separated as a rubbery product by acidifying the potash solution; it reacts slightly acid and it contains only carbon, hydrogen, and oxygen. These facts lead to the conclusion that we are dealing here with rubber oxidation products.

If the values for benzene extract and rubber content are now examined, it will be found that for the most part the dead parts of the tree (wood, bark, cork, etc.) contain considerable amounts of these oxidation products. This indicates that an oxidative decomposition of rubber has already taken place in these parts.

Where does this decomposition process finally lead?

To answer this question, the fruit again appears of fundamental importance. The physiological changes which take place in the endocarp/exocarp system during growth of the fruit deserve most careful attention. In very young fruit, these two elements form one whole: a soft tissue, from which latex flows abundantly when it is wounded. This latex darkens very quickly in the air, and this indicates the presence of oxidation enzymes (see Bobilioff[16]). The rubber obtained from this latex is distinguished from ordinary rubber in that it is extremely soft, even almost plastic. It is, however, insoluble in alcoholic potash and therefore still contains no acidic substances, though the product may contain hydroxy groups. These observations, brought into relation with the strikingly high pentosan content of the endocarp of the more fully grown or mature fruit (E_2 27.41 per cent and F_3 31.80 per cent) and also of the seed coat of the mature fruit (F_2 28.36 per cent) lead to the hypothesis that rubber in the plant organism is transformed into incrusting substances which are built up by C_5 groups, *i.e.*, pentosans, methylpentosans, hemicelluloses, lignins, etc.

In conclusion, particular attention should be paid to another, no less important, analytical result, viz., that the rubber content of the cambium (A_2 and B_2) differs only slightly from that of the soft bark (A_3 and B_3), in spite of the fact that the latter includes the rich rubber-containing latex vessels. If the relatively high rubber contents of petiole (D_6) and green twig (C_1) are considered in connection with this, the route along which the rubber is transported can be seen as it is traced in the tree. Strikingly, this is the normal route also followed by other simpler photosynthetic products, such as sugars, amino acids, etc. How the transport of a strongly apolar high polymer through the cells is possible will be discussed later.

DEVELOPMENT OF A NEW THEORY

As has been outlined, the stages through which rubber metabolism proceeds are: (1) synthesis, (2) transport, (3) polymerization, and (4) breakdown or oxidation.

SYNTHESIS

Where, how, and from what is rubber formed?

Undoubtedly the greatest activity is developed in the leaf of any plant, thanks to the light and heat energy of the sun and to chlorophyll and other extremely active enzymes. Transformations take place in the leaves, and these are impossible in any other parts of the plant, which contain no chloro-

phyll (photosynthesis). Sufficient emphasis cannot be laid on this well known fact.

When Thatcher[17] asserts that "fats containing more carbon and less oxygen in the molecule are a more concentrated form of potential energy than any other group of substances of vegetable origin", he overlooks the isoprene derivatives. As a matter of fact, whereas 125 to 225 cc. of starch or glycogen is capable of yielding 100 kg.-cal. of heat, only about 12 cc. of fats and not more than 5 cc. of rubber would, when oxidized, evolve the same amount of heat, or energy. It follows that much more energy is necessary for the synthesis of isoprene derivatives than for the formation of sugars or fats.

It is, therefore, no coincidence that by far the greater number of rubber- and fat-producing plants grow in the tropics, where the powerful tropical sun puts the plants in a much better position for, or even forces them to, excellent achievement.

These considerations, brought into relation with various observations described in the literature, lead the author to believe that rubber is formed mainly in the leaf and other green parts of the plant.

It is well known that latex from young trees or from young organs of old trees contains rubber particles which are mostly of small size[18]. Hessels was able to prove conclusively[19] that the smaller the size of latex particles, the lower the degree of polymerization of the rubber. In addition, Schoonevelt and Koolhaas[20] stated that the molecular weight of rubber from latex of young trees, amounting to about 60,000, is considerably lower than that of rubber from old trees, *i.e.*, 200,000.

Special attention should be called to the observation of Whittenberger, Brice and Copley[11] and of Rollins, Bailey and DuGruy[12] that rubber in *Cryptostegia* and in goldenrod is found principally in the leaves and other green parts of the plant[21]. Whittenberger and Kelner[22] even stated that "the major portion of the leaf rubber occurs as nonlatex globules in the mesophyll chlorenchyma, entirely distinct from the duct system" and that "these globules are strikingly correlated with the presence of chlorophyll, being largest and most numerous in the palissade cells of fully mature leaves". To these statements the authors added: "The physiological significance of the association of the globules with chlorophyll is not yet known".

In view of this, it is reasonable to assume that rubber and probably all other isoprene derivatives are synthesized mainly in the green parts of the plants. This assumption does not exclude the possibility that rubber is formed without the help of solar energy. In young etiolated germinating plants, for example, such secondary formation of rubber takes place.

In each case, the theory that Hevea rubber is formed in the latex vessels[23] is, in the light of the foregoing, absolutely untenable. Moreover, this theory cannot explain why: (1) rubber is sometimes found outside the latex vessels in such high concentrations (cambium); (2) defoliation has an almost immediate effect on the formation of rubber[24], and (3) the latex vessels, after each tapping, are filled up with rubber so quickly. It is improbable that the rubber content of the latex can be restored so quickly because the rubber must first be formed from starch in the neighboring cells[25].

The question of how and from what rubber is formed now remains.

This question presupposes the hypothesis that rubber is synthesized from another substance, a so-called precursor. Such precursors have been diligently sought[26] and the wealth of information thus brought to light merits admiration.

However, none of the compounds suggested up to the present can reasonably be regarded as a precursor. Meanwhile investigations are being continued.

On what is the hypothesis based that rubber is actually synthesized from a precursor? Undoubtedly on the supposition, generally accepted as correct, that sugars (and not rubber) are the primary products of photosynthetic processes. However, this assumption has never been convincingly proved. Sugars and their polymers, of course, play a very important part in plant life; but isoprene derivatives are not less important. Chlorophyll, *i.e.*, the product with which photosynthesis is closely connected, for example, contains isoprene groups both in its phytol chain and in its nucleus. Furthermore, carotene, xanthophyll, and other pigments containing isoprene groups are present in the chloroplasts, especially in gold-leaved varieties of plants. For these reasons the possibility that in photosynthesis carbon dioxide is reduced directly to isoprene among other products can by no means be excluded.

Conditions for such extremely endothermic reactions are nowhere more favorable than in the leaf, where an excess of energy[27] is present as long as the sun shines, and where this energy can be retained, thanks to the presence of chlorophyll. According to modern ideas of the mechanism of photosynthesis[28], it is possible that carbon dioxide can be reduced, not only to sugars and alcohols, but also to hydrocarbons. In the opinion of Prokofiev[29] it is very doubtful if specific precursors are even formed in the leaves of rubber-producing plants.

For the rest, the possibility of the existence of one or more precursors is left unsettled. Precursors, for example, certainly play a role in the secondary formation of rubber, as mentioned earlier; young etiolated germinating Hevea plants are, therefore, a much better material for the separation and identification of these precursors than are normally growing plants.

TRANSLOCATION

Botanists have proved[30] that, in *Hevea brasiliensis*, photosynthetic products are transported quite normally, *i.e.*, via the sieve tubes. It has, however, been their opinion that rubber is an exception to this, because it is unthinkable that this high polymer, with its pronounced hydrophobic character, should be able to diffuse through the cell wall. Many investigators believe, therefore, that the transport of rubber and even of other photosynthetic products is effected by the latex vessels[31]. Meanwhile numerous objections have been raised against this assumption, the most conclusive[32] being that flow in the latex vessels, if it occurs at all, is only very weak and may take place in both directions[33]. The fact that rubber is also found in high concentration outside the latex vessels, namely, in the cambium, is a further serious argument against transport of rubber through the latex vessels. Moreover, Bobilioff[34] reported that rubber is still formed in a strip of bark which is completely isolated from the bark of the upper trunk. From this and various other facts already mentioned, it is highly improbable that rubber is formed locally in the tissues from easily transportable precursors. Consequently, since rubber occurs in almost every tissue of the (Hevea) plant, transport of rubber through the plant organism must take place.

How can this be explained? Obviously the diffusion process, which is closely related to the permeability of the cell wall complex, depends not only on the nature of the diffusing substance but also on that of the protoplasm membrane and of the interaction between the permeating substance and the

membrane. The structure of the cell wall complex is, therefore, of special interest.

Bungenberg de Jong and Bonner[35] suggested, as the simplest model of the protoplasm membrane, a double film of phospholipoid molecules (see Figure 1). In such a film the outer zones have a pronounced hydrophobic (lipophilic) character, whereas the middle zone, containing the ionized groups, constitutes a hydrophilic zone. In the film there is still room for lipophilic sensitizers, containing at the one end slightly hydrophilic groups, and at the other end chains which are relatively broad and of a length comparable to that of phosphatide chains, *e.g.*, cholesterol, triolein, etc. (see the shaded area in Figure 1B). In Figure 1C the available sensitizer spaces are not completely filled up.

It is clear that the permeability of the membrane model suggested varies with changes occurring in: (1) the length of the fatty acid chains in the phospholipoid molecule; (2) the structure of the lipophilic sensitizer; and (3) the degree of occupation of the available sensitizer spaces, which makes it possible to foresee all possible transitions between films of types A and B.

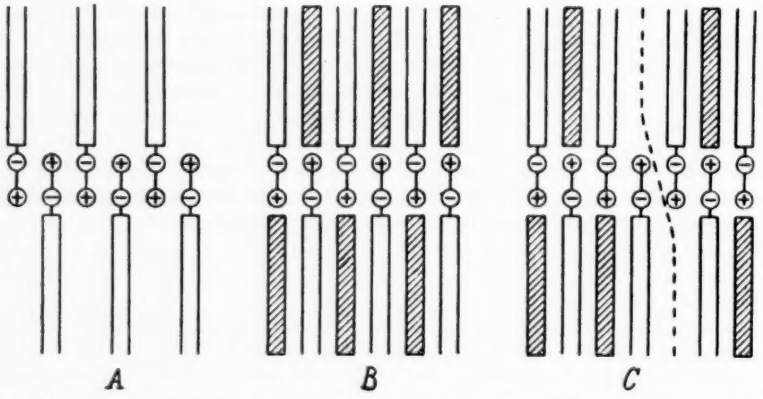


FIG. 1.—Diagrammatic representation of double film consisting of oriented phospholipoid molecules (Bungenberg de Jong and Bonner).

As to the nature of the diffusing substance, *i.e.*, rubber hydrocarbon, it is suggested that this corresponds to that of the membrane just described. To be sure, phospholipoids occur in Hevea latex in relatively high concentration[36] because they diffuse into the latex vessels together with the rubber. In nature, phospholipoids take first place together with the proteins as wetting agents, detergents or emulsifiers: the lipophilic chains of the higher fatty acids on the one hand, and the hydrophilic phosphoric acid and choline or colamine on the other, make these compounds highly suitable for this purpose (see Figure 2). Moreover, it has been repeatedly stated that vegetable phospholipoids are bound to sugars and inositol derivatives[37], which means a strengthening of the hydrophilic part of the molecule. The phospholipoids from Hevea latex apparently occur in the form of complexes containing proteins, sterols and sugars[38]. Such complexes have been found in several other natural products[39].

Besides functioning as detergents, phospholipoids have another important function in that they protect the vulnerable isoprene chain against oxidation during transport through the plant. In this connection some of Süllmann's papers are worthy of attention[40]. According to this investigator the enzyme

lipoxidase can oxidize carotene to a colorless compound provided that unsaturated fats are present[41]. It has been further established by Süllmann that lecithins have a checking influence on the said oxidation process, provided again that unsaturated fats are present; unsaturated fat acids on the contrary weaken or impede this checking action. Thus, if lecithins have a protective action on carotene, they also have one on rubber as another isoprene derivative.

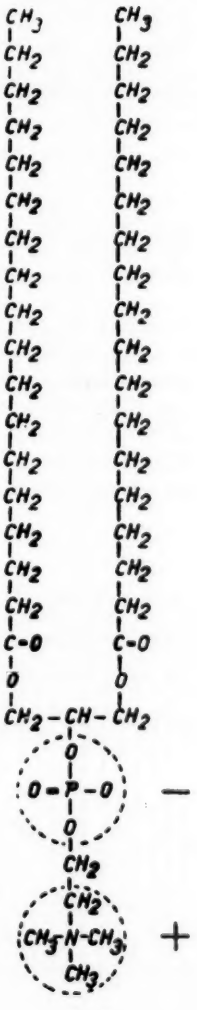


FIG. 2.

Assuming (see below) that freshly synthesized rubber is a liquid, the theory according to which the lipophilic polymer is transported through the plant in the form of a highly dispersed oil-in-water emulsion, in which the rubber droplets are surrounded by a monomolecular layer of phospholipoide molecules, is very attractive. This means not only a maximum protective action by a

minimum quantity of phospholipoid but at the same time forms a system which is almost ideal for furthering quick diffusion through the cell wall. This picture probally represents the solution of an old, still unsolved problem, *i.e.*, the physiological function of phospholipoids in life processes. Since phosphatides are components of all living cells, this concept explains the possibility of translocation of every lipophilic substance through those cells, *casu quo* through the living organism, irrespective of whether it is animal or vegetable in origin.

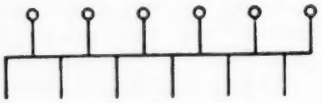


FIG. 3.

Confirmation of the theory concerning the transport of rubber in the plant can be found in various statements made by investigators who have studied the mechanical structure and chemical composition of the rubber globules in latex.

It was established by Kemp[42] and by Hendricks, Wildman, and McMurdie[43] that many globules, particularly of the smaller ones, contain a liquid; according to Hendricks and coworkers these globules may even flow into each other. This observation explains in part the occurrence of the pear-shaped globules mentioned by many investigators[44]. The elongation of the originally spherical particles, however, might also be ascribed to a deformation of the rubber droplet caused during and after tapping when there is an intensive flow of the latex in the narrow vessels[45].

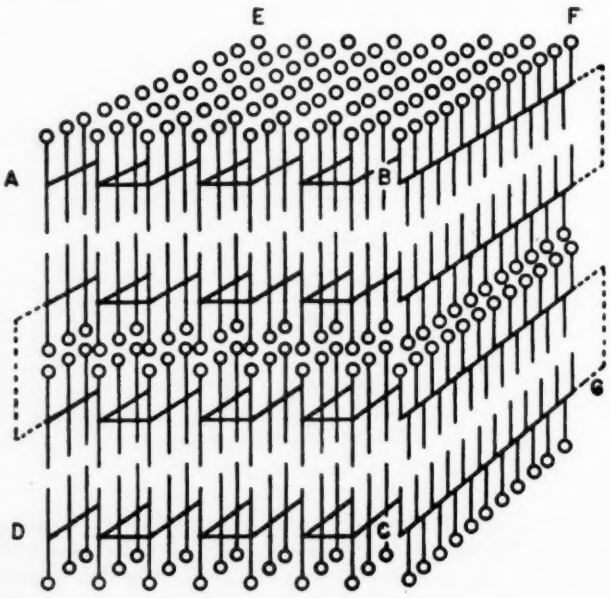


FIG. 4.

As to the surface layer of the latex particles, it has been postulated that this must be constituted of lipoprotein complexes[46]. Such layers have also been found on the surface of the fat globules in milk[47] and other naturally occurring particles[48].

As an instructive illustration of the theory of the transport of rubber, the formation of latex in the plant will now be discussed.

It is known that latex serum contains proteins in solution. How do the liquid rubber droplets just diffused in the latex vessel behave in this protein medium?

The work of Astbury[49], Pauling[50], Dervichian[51], and Palmer[52] shows that the peptide chain is built up from amino acids in such a way that the side chains of the polar amino acids are projected out on one side of the peptide chain and the nonpolar side chains on the other (see Figure 3). Palmer on various grounds suggested a model for egg albumen molecule which consists of four superimposed layers with three interfaces, one polar and two nonpolar (Figure 4). Under favorably chosen conditions such protein micellae can unfold and form a monolayer. The possibility of spreading proteins[53], for example, is based on this.

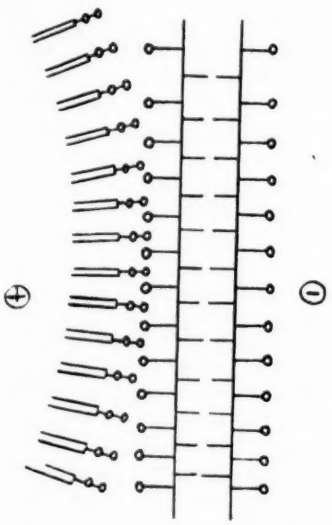


FIG. 5a.

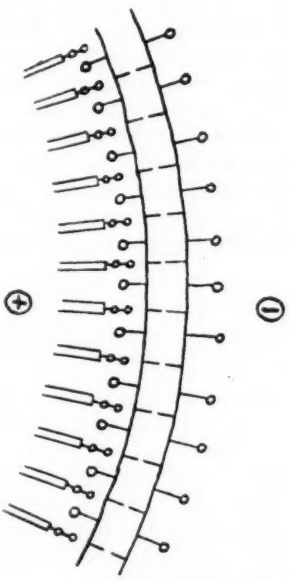


FIG. 5b.

When a rubber droplet which has just penetrated through the wall of the latex vessel comes in contact with such a protein micella, there is every reason to assume that the polar parts of the phospholipoids on one side, and those of the proteins on the other, attract each other and bring about an arrangement as represented in Figure 5a. The attraction between the two particles may, moreover, be promoted by the fact that the electrical charges of both particles are opposite. As a matter of fact, since the pH of latex is about 6, all amphoteric substances with an isoelectric point below 6 (proteins) are negatively

charged, and those which have an isoelectric point above 6 (lecithins) are positively charged[54].

In Figure 5b the protein molecule follows the rounding of the rubber droplet, and thus fulfills the effort to unite the polar parts of the molecules as completely as possible. This effect obviously must lead to the complete unfolding of the protein molecule in such a way that the latter comprises two superimposed layers, with one lipophilic inner zone and two hydrophilic outer zones, one of which is turned toward the aqueous latex medium. This configuration brings a new and very important factor into play since through the peptide chain, the film now gains a mechanical transverse connection which undoubtedly results in a considerable increase in the stability of the surface layer of the rubber droplet[55].

In the phenomena just described the dimensions of the rubber droplets and protein micellae are not of prime importance. If necessary, more than one protein molecule joins with only one rubber droplet until the latter is completely covered with protein and, consequently, exercises an attraction on new rubber droplets entering the latex vessel. Contact between these two kinds of rubber droplets forms the well known latex particles, the content of which, at least in the beginning, is liquid. Depending on the constitution of its surface layer, the young latex particles adsorb proteins or phospholipoids from the surrounding protein micellae and rubber droplets, respectively. This growing process of the latex particles can continue *ad infinitum* as long as rubber droplets are available. For the rest, direct coalescence of rubber droplets with old latex particles may also take place, provided that the electrophoretic charges of the two kinds of globules are favorable. It is, therefore, understandable that (1) the surface layer of the latex particles, although always constituted of a phospholipoid/protein complex, can vary from particle to particle; (2) the size of latex particles varies so widely; and (3) the white and yellow fractions obtained from fresh Hevea latex[56] have properties which differ noticeably.

POLYMERIZATION

It has already been pointed out that many rubber globules, particularly small ones, *i.e.*, those occurring abundantly in young trees or young organs of old trees, contain a liquid. In addition, it has been established[57] that ordinary latex also contains rubber particles which have a solid content; these particles are of larger size, and occur mainly in old trees and organs. Mashtakov[58] has presented evidence that the degree of polymerization of rubber in kok-saghyz increases as the plants mature. From these facts the conclusion can logically be drawn that the liquid rubber gradually changes into solid rubber. Intermediate stages in which the rubber is in a more or less viscous liquid state have also been described[59].

Flint[60] refers to the hypothesis that the rubber hydrocarbon is present in the liquid state and in a low degree of polymerization in the tree, and that at a definite time the degree of polymerization increases, starting at the surface of the particles and progressing into the interior. The conclusion of Hessels[19] that there is a relation between particle size and degree of polymerization deserves special attention. Discussing the possibility that this relation can be explained by the mechanism of bead polymerization, this author remarked that, in a polymerization reaction, the length of the chains depends in large measure on the rate of the reaction[61]. At elevated temperatures or with a very active catalyst, the rate of the reaction is high, and to a great extent short chains are

formed, whereas if the reaction is slow, long chains are formed. As a consequence, if polymerization commences at the surface of the rubber particles under the influence of a catalyst in solution in the serum[62], the rate of polymerization of small particles, which have a larger surface area than that of an equal volume of large particles, is greater and the resulting chains are shorter.

However, in the light of the present author's concepts as to the formation of latex, the relation between particle size and degree of polymerization is satisfactorily explained by the fact that small particles are "young" and therefore contain rubber in a lower degree of polymerization than the rubber of "old" large particles, which have taken part in the polymerization process over a longer period of time.

Considering these facts, the conclusion seems justified that, at least in *Hevea brasiliensis*, polymerization takes place mainly in the latex vessels. This is emphasized again by the fact that conditions in the latex are almost ideal for promoting bead polymerization, to wit: (1) the best stabilizers and emulsifiers are present; (2) the viscosity is neither too high nor too low; (3) the densities of the dispersed substance and external phase differ only slightly; (4) the temperature is low[63]; (5) the pH is very favorable to polymerization[64] and remains practically constant, as latex is an almost perfect buffer solution; and (6) peroxides and other per compounds, including oxidized rubber[65], which function as polymerization catalysts, are present.

OXIDATION

As already mentioned, the supporters of the theory that rubber is a waste product base their belief mainly on (1) a supposed inertness of the rubber hydrocarbon, and (2) the presence of rubber in old fallen *Hevea* leaves.

The latter argument is immediately invalidated by the experimental fact that old fallen leaves of Hevea contain more protein (2.03 per cent) than rubber (1.88 per cent). And does anyone doubt the food value of proteins?

As to the inertness of rubber, it is a well known fact that purified rubber quickly becomes tacky in the air, particularly when the rubber contains traces of copper, and enzymes capable of breaking down rubber must exist because rubber is attacked by many microörganisms[66].

If the oxidative decomposition of rubber in the living cell is improbable or even impossible[67], those compounds which are usually assumed to oxidize in respiration processes, *e.g.*, sugars, amino acids, ethyl alcohol, etc., are incapable of reacting with free oxygen outside the plant, and thus are as inert as rubber. The fact that these compounds nevertheless oxidize in the living cell must be ascribed to the presence of powerful enzymes[68]. On the basis that oxidases are present in latex, Spence[69] suggested that rubber can be broken down in the plant into simple assimilable products, such as sugars. In this connection the possible presence of lipoxidase in rubber-producing plants should again be pointed out. If carotene, as an isoprene derivative, even more resistant than rubber because of its protecting end groups, can be decomposed by the intervention of lipoxidase, decomposition of rubber by means of this enzyme is equally possible.

With all these facts in mind it is absurd to believe seriously in the inertness of the rubber hydrocarbon Moreover, the present author's analyses show that oxidation products of rubber are present in various parts of the *Hevea* tree.

Thus, it seems a well established fact that rubber is broken down in the plant. However, the question of the purpose of this oxidation still remains.

It has been suggested that the breakdown of rubber must lead to the ultimate formation of all those incrusting substances which have a C_5-chain skeleton, *i.e.*, pentosans, hemicelluloses, lignins, etc. This hypothesis is based on certain remarkable values obtained in the analysis of the fruit in its different stages of growth. Strong confirmation of the theory was obtained, in addition, by a vast amount of experimental data, which show a definite relation between the presence of rubber and the formation of the incrusting substances.

(1) The latex vessels in the leaf of *Hevea brasiliensis* follow very closely the veins of the leaf[70]. In *Cryptostegia* varieties, Whittenberger and his coworkers[11] showed convincingly that rubber-bearing substances of the chlorenchyma are most numerous in areas adjacent to the veins (see Figure 6).

(2) Untapped trees increase in circumference more quickly than trees which are regularly tapped[71].

(3) The formation of rubber decreases when the tree begins to bear fruit[72].

FIG. 6.

(4) Trees with great resistance to wind are, in general, poorer rubber producers than trees with little[73] such resistance.

(5) During the period in which new tissue is formed in the guayule plant, the rubber content falls noticeably[74].

(6) According to Kostytschew and Went[75] rubber deposition in general takes place most vigorously in mature tissues. Thus seedling guayule plants accumulate a smaller proportion of rubber than do older plants, while in koksaghyz rubber formation occurs principally in the mature root. The rubber content of latex from young rubber trees or from young parts of the tree is less than that of latex from mature trees. In this connection attention should be called to the finding of De Vries[76] that the plasticity of raw rubber depends on the age of the tree from which the rubber is obtained; the younger the tree, the more plastic is the rubber obtained.

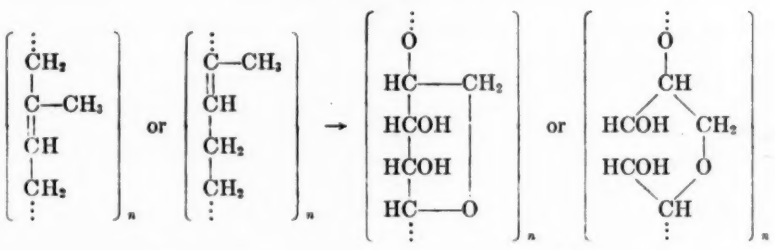
(7) Very heavy tapping often causes the appearance of brown bast disease in *Hevea* trees, which is characterized by an abnormally extensive formation of

stone cells[77]. In the opinion of the author, brown bast disease must be regarded as a physiological reaction against too heavy losses of rubber: the plant tries to put its reserve food, rubber, in safety by transforming it as much as possible into the products for which it is intended, *i.e.*, pentosans, etc.

At this point attention should be called to experiments by McGavack and his coworkers[78]. When, during starvation, kok-saghyz roots were periodically extracted with toluene, these investigators found that the amount of toluene extract increased steadily with the period of storage (up to 72 days). This fact would be at variance with the concepts of the present author only if the toluene extract consisted wholly of pure unoxidized rubber. It is doubtful, however, whether this was so. Furthermore, in sampling and extracting their plant material, McGavack and his coworkers did not take the necessary precautions to prevent oxidation of the rubber hydrocarbon.

In conclusion, a few words may be added as to the mechanism of the oxidation of rubber. Referring to the most instructive work of Farmer and his coworkers[79] and to the summarizing article by Dogadkin[80], the conversion of rubber into pentosan may be schematically represented by the following equation:

$$(C_5H_8)_n + 2n\,O_2 \rightarrow (C_5H_8O_4)_n$$



rubber pentosan

In such a complex reaction various intermediate products and byproducts must be formed. The fact that, in practice, none of these have been identified must be ascribed to the fact that no serious investigation in this direction has ever been made. Meanwhile, the present author[38] observed that beautiful crystals of two organic magnesium salts occur abundantly in *Hevea* latex, to which the following empirical formulas may be ascribed:

(1) $C_5H_6O_7Mg \cdot 3H_2O$
(2) $C_7H_8O_7Mg \cdot 2H_2O$

Both compounds can be regarded as oxidation products of rubber. It is not difficult to imagine compound (1) as derived from pentosans. As occurs so often in nature, the element magnesium acts as a carrier for acid-reacting products, thus rendering them innocuous. As for compound (2) the impression is had that this is in some way related to quebrachitol, which is present in relatively high concentration in *Hevea* latex. Perhaps quebrachitol units are present in the long isoprene-chain of the rubber molecule. It is, however, beyond the scope of this article to discuss this subject in detail.

Attention should also be paid in this connection to the so-called acetone-extract of rubber. Although, on the one hand, the nitrogen and ash contents

of rubber can easily be reduced considerably by purification, such as by creaming, centrifuging, boiling with lye, protein-splitting bacteria and enzymes, etc., removal of acetone-soluble components by such processes never appears to be completely successful. It can be concluded that most of the acetone-soluble substances occur in the interior of the rubber globules and therefore cannot be eliminated by the purification processes mentioned. As is known, the acetone extract contains, among other products, rubber oxidation products[81]; hence a more profound chemical analysis of the acetone extract, aimed at the separation and identification of rubber oxidation products should certainly be successful. The so-called resins which occur abundantly, for example, in the latex of *Hevea* trees that have never been tapped[82] also contain oxidation products of the rubber hydrocarbon[83].

DISCUSSION

Although the theory just developed is based to a great extent on exact analytical data, it nevertheless remains a theory and, as such, contains a number of hypotheses which can only be tested and verified by further experiments.

As for the synthesis of rubber, on the one hand, it would be of fundamental importance if plant physiologists accurately investigated again the principles of photosynthesis to ascertain whether C_6-compounds and C_5-compounds can be equally well formed directly from carbon dioxide. On the other hand, etiolated germinating plants form the most promising starting material for the successful separation and identification of rubber precursors because, in these plants, direct photosynthesis of rubber is completely excluded and therefore cannot interfere with the formation of rubber via precursors.

The concept of the translocation and polymerization of rubber would certainly find very strong support if liquid rubber could be isolated from the living plant. This might be done, for example, by sampling latex from the interior of the plant according to a method described by Houston[83].

Finally, it is far from simple to prove that rubber is actually transformed into incrusting substances. As far as can be ascertained, no experimental observation contradicts the theory; moreover, the formation of pentosans from rubber has not been established in a convincing manner. Nevertheless, a profound chemical analysis of, for example, the acetone extract of rubber or of the latex from *Hevea* trees which have never been tapped, will render valuable information about the course of the reaction under investigation.

SUMMARY

Systematic analysis of the latex of *Hevea brasiliensis* yielded results which induced the author to study the metabolism of rubber more closely. As it was realized that the latex picture alone would not lead to sound conclusions about the formation and breakdown of rubber, analysis of the whole Hevea tree, from the highest leaflets down to the very root tips, seemed desirable. For practical reasons, however, such a profound investigation had to be reduced to the analysis of only the most important parts of the tree. The various analytical results obtained have forced the author to make a radical revision of some of the current concepts.

For several reasons the synthesis of rubber probably takes place mainly in the green parts of the plant, and principally directly from carbon dioxide. The possibility of the formation of rubber from precursors (secondary formation) is still uncertain. Such formation, for example, must proceed in etiolated germinating plants. Freshly synthesized rubber is present in the plant in the liquid state.

This liquid rubber is translocated through the plant in the form of a highly dispersed oil-in-water emulsion, in which the rubber droplets are surrounded by a layer of a phospholipoid complex. As an instructive illustration of this hypothesis the formation of latex is discussed.

The process of polymerization results in the transformation of the liquid rubber into the solid phase; this solid rubber is deposited everywhere in the plant. It appears most probable that, in *Hevea brasiliensis*, polymerization takes place mainly in the latex vessels.

The breakdown of rubber, finally, is proved to be an oxidation process. For several reasons there is cause for believing that oxidation of rubber in the plant leads to the formation of those incrusting substances which are built up by C_5-groups, *i.e.*, pentosans, hemicelluloses, lignins, etc.

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THE HEAT SENSITIVITY OF HEVEA LATEX. III. THE PROCESS OF HEAT SENSITIZATION OF LATEX WHICH HAS BEEN DEGRADED BIOCHEMICALLY *

FRANCIS LEPETIT

FRENCH RUBBER INSTITUTE, 42 RUE SCHEFFER, PARIS, FRANCE

In the previous part of this investigation[1], it was shown that it is possible, by the simple addition of zinc oxide, to degrade the stabilizing agents in ammoniated latex and to render the latter sufficiently heat sensitive for it to be applicable to the manufacture of molded goods. This can be accomplished by allowing the latex to age naturally, by thermal treatment or, finally, by a more practical method involving the action of proteolytic enzymes, as already shown in the present investigation[2]. When trypsin from powdered hog pancreas is used as the agent, the sensitized latex mixture gels rapidly at ordinary temperature, and although this premature coagulation can be applied to cold molding, in other cases it so interferes with operations that the same inconveniences found in the Kaysam process are encountered. There remained, accordingly, the alternative of studying the process of heat sensitization by agents such as trypsin, with a view to extending the time which sensitized latex mixtures can be kept successfully and to developing the process to a point where it is applicable on an industrial scale.

DIFFERENCES IN THE BEHAVIOR OF OLD LATEX AND LATEX TREATED WITH TRYPSIN IN THE PRESENCE OF ZINC OXIDE

Although depending on the same principle, the biochemical degradation of ammoniated latex differs somewhat from the degradation resulting from natural aging in that the characteristics of biochemically treated latex are different from those of naturally aged latex.

TIME OF PRESERVATION

Comparative measurements show that, for a given length of time of coagulation at a given temperature, *e.g.*, at 50° C, latex six years old keeps longer, *i.e.*, several weeks, at room temperature when it contains zinc oxide than does latex treated with trypsin, which keeps only several hours to two days, depending on conditions.

The development of heat sensitivity during storage is likewise more rapid in trypsinated latex than it is in old latex, and the coagulation of old latex is accelerated relatively more by heat treatment than is the coagulation of latex containing trypsin by the same heat treatment.

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INFLUENCE OF DILUTION

Another difference between naturally aged latex and trypsinated latex is to be found in the influence of dilution. The curves shown in Figure 1 were obtained by diluting each latex with increasing proportions of distilled water, and measuring, after each dilution, the heat sensitivity at 70° C. In the case of old latex, dilution has no effect on the heat sensitivity down to a concentration of rubber of about 26 per cent, below which the heat sensitivity disappears abruptly. In the case of trypsinated latex, the heat sensitivity decreases slowly at first as a function of the dilution, then more rapidly as the concentration of rubber approaches 47 per cent. The latter latex is, therefore,

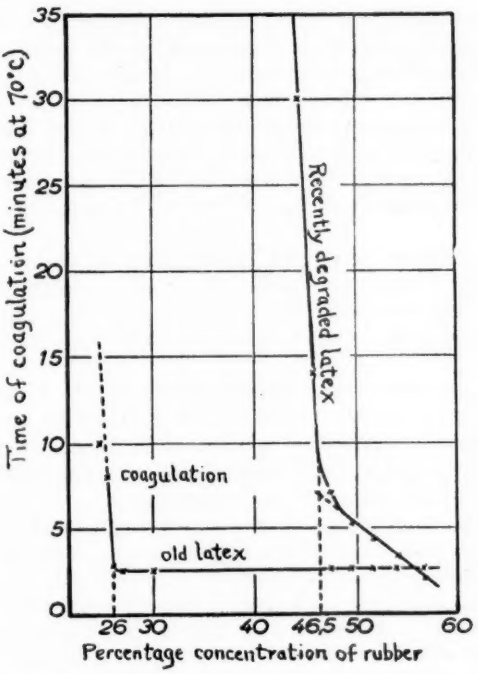

FIG. 1.—Effect of dilution on the heat sensitivity of old latex and of trypsinated latex.

affected more by dilution than is naturally aged latex. If trypsinated latex is diluted with distilled water to the point where it is no longer heat sensitive, and is then creamed again, a concentrated latex is obtained, but this time the latex is no longer heat sensitive, even after readjustment of the ammonia content. In this second creaming operation, part of the serum is removed and replaced by water. Consequently, in virtue of certain of its components, notably its ammonium salts, serum must be present to assure the coagulation of degraded latex containing zinc oxide.

SEPARATION AND COMBINATION OF CREAMS AND SERA

With a view to correlating the heat sensitivity of latex with its composition, the cream and serum phases obtained from undegraded latex, from latex de-

graded by trypsin, and from old latex were separated and examined. These four samples comprised the following types:

(1) Ammoniated latex, creamed to 59.5 per cent rubber content, six months old, and not heat sensitive.

(2) The same as the first latex, but degraded with 0.1 per cent of commercial powdered degreased hog pancreas by digestion for three days at 18° C. In the presence of zinc oxide, this latex coagulated in two hours at 18° C and in three minutes at 50° C.

(3) Old ammoniated latex which had been preserved for six to seven years. In the presence of zinc oxide, this latex coagulated in two to three months at 18° C and in sixty minutes at 50° C.

It was not practicable to separate cream and serum by centrifuging because this procedure entailed the risk of coagulating the degraded latices, which because of their instability, were sensitive to frictional forces. It was considered preferable to operate by creaming, although the creaming agent in some cases hindered the subsequent operations. From a practical standpoint, two successive recreamings by methylcellulose, each preceded by dilution to 35 per cent rubber content, which eliminated 88 per cent of the original serum, were sufficient to separate the major portion of the soluble substances from the cream.

Because of appreciable amounts of methylcellulose still present, the creams which were separated were very thick. Their ammonia content was adjusted to 0.6 per cent. The sera were then concentrated on a steam bath so that, when mixed later with the creams, the concentrations of the latter would not be lowered.

Action of sera on their corresponding creams (Table 1, first series).—The three creams separated from the three degraded latices did not coagulate when heated in the presence of zinc oxide. But when they were mixed with their corresponding sera, they were again heat sensitive. This shows the important role played by certain components in the serum.

Action of the serum of normal latex on creams of degraded latex.—The next question was to ascertain which phase, the cream or serum, undergoes degradation and as a result becomes heat sensitive. To settle this question, the same serum from normal latex was mixed with the different creams from the degraded latices. As will be seen from Table 1 (second series), the serum of normal latex made all the creams from the degraded latices heat sensitive; it contained in its natural condition, therefore, sufficient ammonium salts to coagulate a more stable cream.

Action of sera of degraded latices on cream from normal latex (Table 1, third series).—When degraded to a sufficient degree, serum makes normal cream heat sensitive, but to a lesser degree than in the preceding case since, on the one hand, serum moderately degraded by trypsin (0.1 per cent) has no heat sensitizing action and, in addition, the times of coagulation of the other mixtures are longer under these conditions. Consequently the heat sensitizing action of degraded cream is greater than that of serum.

Action of sera of degraded latices on the creams of degraded latex (Table 1, fourth series).—In these cases the times of coagulation, both when hot and at ordinary temperature, were shortest.

In summary, for ammoniated latex to become heat sensitive, it is necessary first of all that the serum, or at least certain of its components, be present and, secondly, that one of the phases, cream or serum (and *a priori* both) be de-

TABLE 1

HEAT SENSITIVITY OF RECONSTITUTED HEVEA LATICES

Series no. 1. Serum with its corresponding cream.
Series no. 2. Normal serum with cream from degraded latex.
Series no. 3. Serum from degraded latex with normal cream.
Series no. 4. Serum from degraded latex with cream from degraded latex.

Series	Latex reconstituted by serum + cream	Time of coagulation in presence of zinc oxide: minutes at 70° C	Time of coagulation in presence of zinc oxide: at ordinary temperature
1	normal + normal	>30	1 mo.
	0.1% trypsin + 0.1% trypsin	5.5	24 hrs.
	0.5% trypsin + 0.5% trypsin	0.75	0.5 hr.
	old + old	1.5	6 days
2	normal + 0.1% trypsin	30*	12 days
	normal + 0.5% trypsin	1.5	6 hrs.
	normal + old	8	16 days
3	0.1% trypsin + normal	>30	>1 mo.
	0.5% trypsin + normal	8	20 days
	old + normal	11	>1 mo.
4	0.1% trypsin + 0.1% trypsin	5.5	24 hrs.
	0.1% trypsin + 0.5% trypsin	0.75	1 hr.
	0.1% trypsin + old	3.5	12 hrs.
	0.5% trypsin + 0.1% trypsin	2.5	15 hrs.
	0.5% trypsin + 0.5% trypsin	0.75	0.5 hr.
	0.5% trypsin + old	2.25	9 days

* Partial coagulation.

graded. Accordingly whether brought about by the biochemical method or by natural aging, degradation changes the two phases in latex; acidic products are formed in the serum and the cream is rendered more unstable and more sensitive to the action of a relatively small amount of coagulating agents. These two points have been definitely established by an examination of the properties of sera and creams separated by repeated creaming.

EXAMINATION OF SERA AND CREAMS

SERA

The presence of acidic substances in the serum of degraded latex was proved chiefly by determinations of the KOH value and by the partial solubilization of zinc oxide which had previously been added. These determinations were carried out with crude sera prepared from the first repeated creaming and with the same sera after having been concentrated to one-third their weights, *i.e.*, brought to the 59 per cent concentration of the original latex.

Content of acidic substances.—The serum was treated with an excess of formaldehyde, which combines with free and combined ammonia. The NH_2 groups of the amino acids are likewise fixed, so the CO_2H groups can be titrated with potassium hydroxide.

The data in Table 2 (first series) show that, when latex becomes degraded, the content of acidic substances in the serum increases. Allowing for experimental errors, the KOH number should be about three times as high in con

TABLE 2

Series no.	Determinations	Serum: Normal	Serum: 0.1% trypsin	Serum: 0.5% trypsin	Serum: Old
1	KOH no.* of crude serum	155	165	244	316
	KOH no. of serum concentrated to ⅓ weight	400	500	750	740
2	Zinc dissolved in crude serum (per cent)	0.019	0.025	0.044	0.025
	Zinc dissolved in concentrated serum	0.088	0.113	0.188	0.110
3	$\left(\frac{\text{g.-mol. KOH}}{\text{g.-mol. Zn dissolved}}\right)$ for crude serum	9.5	7.6	6.4	14.7
	$\left(\frac{\text{g. 1-mol. KOH}}{\text{g.-mol. Zn dissolved}}\right)$ for concentrated serum	5.3	5.1	4.6	7.8

* Expressed as mg. of KOH per 100 g. of serum.

centrated sera as in original sera. This was found to be true of sera from latex degraded by fermentation; however, for serum from normal latex and in particular for serum from old latex, this ratio was less than three, and this indicates the presence of unstable ammonium salts, such as ammonium carbonate, which would be expected to decompose during concentration of the serum.

To show the relationship between the content of acidic substances in the serum and the heat sensitivity of the latex, the changes in these two factors as functions of the time of digestion were followed. Figure 2 shows the results. The heat sensitivity appears to become appreciable at a well defined value of the KOH number, then to increase with it, and finally to remain practically constant after five or six days of digestion.

Content of dissolved zinc in serum.—An increase in the content of acidic substances in serum can be responsible for the heat-sensitizing effect only through the intermediary action of zinc salts formed from the zinc oxide added. To estimate the part played by zinc salts, the zinc ion was determined volumetrically by the mercuric thiocyanate method[4], with which it is possible to determine 0.3 to 15 milligrams of zinc with a precision of 0.2 milligrams. One-

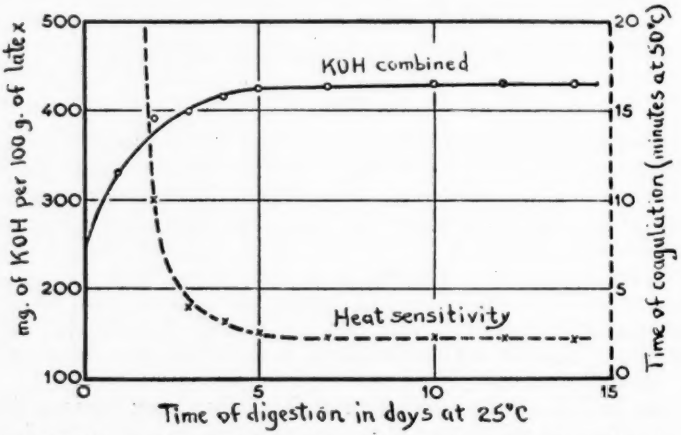

FIG. 2.—KOH index and heat sensitivity as functions of the time of digestion of latex treated with 0.2 per cent of powdered hog pancreas.

half gram of a 33 per cent dispersion of zinc oxide was added to 10 cc. of serum; after allowing to stand for one hour, the excess of zinc oxide was separated by centrifuging, the centrifuged serum was incinerated, and its zinc content determined.

The quantity of zinc dissolved by serum increases with the degree of degradation of the latex (see Table 2, second series). Concentrated sera dissolve relatively more zinc oxide than the original crude sera because solubilization of the zinc oxide by the ammonium salts is a reversible reaction which is influenced by hydrolysis.

To confirm the fact that the heat-sensitizing effect is due to zinc in solution, sera which had been in contact with zinc oxide for one hour and had then been centrifuged were added to highly degraded cream. The results are shown in Table 3.

TABLE 3

ACTION OF SERA CONTAINING ZINC IN SOLUTION ON A HIGHLY DEGRADED CREAM

Composition of the mixture	Time of coagulation at 70° C (minutes)	
	Zinc absent	Zinc present
Normal serum (0.088% zinc) + cream containing 0.5% trypsin	25	1.5
Serum containing 0.5% trypsin (0.188% zinc) + cream containing 0.5% trypsin	1.5	0.75

In both cases, the heat sensitivity reappeared when no zinc oxide had been added. Nevertheless the times for coagulation to take place were longer than when zinc oxide had been added, for the latter must dissolve during the heating and thus accelerate coagulation.

Relation between the content of acidic substances and quantity of zinc dissolved in serum.—The ratio: $\frac{\text{g.-mol. of KOH}}{\text{g.-mol. of dissolved zinc}}$ of original normal sera is higher than that of concentrated sera, *i.e.*, for a given content of acidic substances and for a given time of contact with zinc oxide, normal sera dissolve less zinc oxide than do concentrated sera. Dilution therefore decreases the capacity of serum to dissolve zinc oxide.

If the values of this ratio are classified, they will be found to fall in the same order, whether they represent normal sera or concentrated sera. In view of the fact that zinc salts are not formed instantaneously because of the reactions taking place in heterogeneous phases, a definite amount of zinc oxide should be dissolved at the end of a more or less extended time, depending on the acids present in the serum. On the assumption that solution is completed, the ratio:

$$\frac{\text{gram-moles of KOH combining}}{\text{gram-moles of zinc dissolved}}$$

should be equal to 2, irrespective of the factor n of ammonia in the complex, since zinc is bivalent:

$$2\,NH_4X + ZnO + (n-2)NH_3 \rightleftarrows (NH_3)_nZnX_2 + H_2O$$

The fact that the experimental values are larger indicates that equilibrium was not reached in one hour of contact with zinc oxide at ordinary temperature. The lowest values, *i.e.*, those representing the closest approach to equilibrium, are for latices degraded by trypsin, which have been shown to coagulate rapidly when cold.

CREAMS

The experiments with combinations of creams and sera showed that each cream behaved differently with respect to a given serum, so that a comparison of their essential properties was obviously necessary. Nitrogen determinations and alcoholic extractions of the crude rubber obtained by evaporating creamed latex were carried out by the method described by Baker[5].

TABLE 4

IMPORTANT CHARACTERISTICS OF CREAMS FREED OF SERUM

Series	Determinations	Cream			
		Normal	0.1% trypsin	0.5% trypsin	Old
1	Nitrogen in the rubber (%)	0.18	0.15	0.10	0.13
2	Alcohol extract (% of the rubber)	3.15	3.28	3.33	2.56
	Acid number (mg. of KOH per 100 g. of rubber)	140	220	280	180
	Alcohol extract soluble in ether (% of the rubber)	2.46	2.53	2.75	2.02
	Acid number of this extract	115	160	225	155
3	Time of coagulation in presence of zinc oxide + ammonium sulfate Temp. 26°	4 days	60 min.	6.5 min.	12 hrs.
	50°	39 min.	11 min.	1.25 min.	12 min.
	70°	2.75 min.	2.25 min.	—	1.75 min.

Nitrogen content.—The major part of the nitrogen content of the cream is combined with, and adsorbed by, the rubber globules, for the other nitrogenated compounds are found in the serum which has been separated. The greater the degree of degradation, the lower the nitrogen content of the cream, in conformity with the mechanism of the process as described. The most highly deproteinized creams correspond to sera containing the highest content of acidic substances.

Alcoholic extraction.—Ammonium salts of fat acids are capable of being adsorbed jointly with the proteins, but contrary to the latter, the former are soluble in alcohol and the two can therefore be separated.

According to Table 4 (second series), the alcoholic extract increases slightly during fermentation, although remaining within its normal values. The acid number shows that the amount of soaps increases during fermentation and that they tend to replace the degraded proteins. Baker[5] has pointed out that the fraction of the alcohol extract which is soluble in ether contains all the substances associated with the rubber phase. In this case the major part of the components of the alcohol extract are in the adsorbed state, since the ether extract and its acid number correspond to approximately 80 per cent of the alcohol extract and its acid number, respectively. The fraction soluble in ether was analyzed only roughly because of the very small quantity available; unsaturated fat acids such as oleic acid were the chief products identified.

Apparently a portion of these fat acids are formed during degradation by hydrolysis of the lipides and of lipoprotein compounds present in the latex. Actually powdered hog pancreas contains, in addition to trypsin, other diastases, among which is a lipase whose presence may lead to secondary reactions. It should be noted that Baker[6] and Altman[7] likewise observed the formation of soaps during the storage of ammoniated latex.

Heat sensitivity of creams.—By incorporating in creams a given percentage of zinc oxide and ammonium sulfate (5 grams of cream + 0.25 gram of a dispersion of 33 per cent zinc oxide + 0.5 cc. of a normal solution of ammonium sulfate), it was possible to measure accurately the true times of coagulation of the creams, since under these conditions the times were no longer influenced by the ammonium salts from the serum, and thus to estimate, by reference to cream from normal latex, the extent of degradation of the other creams.

According to the data in Table 4 (third series), creams of degraded latex coagulate much more rapidly than does the cream of normal latex. Consequently degradation has some sort of effect on the stabilizing compounds adsorbed by the rubber particles, whereby the cream is rendered more sensitive to coagulation. In other words, the more degraded is a cream, the smaller is the percentage of coagulating agent necessary to bring about coagulation at a predetermined temperature and in a predetermined time.

DISCUSSION OF THE RESULTS

Although during separation of the two phases, the repeated dilution and creaming had a tendency to cause desorption and to change to a certain extent the partition of some of the components between cream and serum, the results described above are still comparable and indicate that three distinct processes take place.

(1) Biochemical degradation of proteins partly adsorbed by the rubber particles takes place, with formation of a small quantity of acidic products, which remain in the serum as ammonium salts.

(2) These acidic substances function as sensitizing agents in that they solubilize part of the zinc oxide and form ammonium zinc salts, which promote coagulation.

(3) The hydrolyzed proteins are removed from the surface of the rubber particles and are replaced chiefly by ammonium soaps. The greater the extent of this deproteinization, the more sensitive is the cream to coagulation.

Consequently the intrinsic heat sensitivity of a degraded latex depends on the progress of two reactions:

(1) the increase in the ionic strength of the serum by formation of positive ions in low concentration;

(2) qualitative and quantitative changes in the stabilizing agents, which are manifest in a decrease in the charge on the rubber particles and a change in solvation.

The first action is general and is indispensable for coagulation to take place; even when highly degraded, a cream is not heat sensitive if the acidic substances of its serum have been eliminated. The second action is less general than the first, for it does not take place directly if the ionic strength of the serum predominates. But if this ionic strength remains small because of the presence of a very small quantity of acids, the decrease in stability of the cream becomes indispensable to the effectiveness of the low concentration of coagulant ions in the serum. This is the reason that a normal latex is not heat sensitive, even when its serum contains a small amount of acids, and even when a highly degraded cream is rendered heat sensitive by this serum (see Table 1, second series). It is possible to avoid washing the coagulum only by starting with a low concentration of ammonium salts, and such a low concentration is then

insufficient for the Kaysam process to be applicable. Degradation of the stabilizing substances is in this case indispensable to make up for the deficiency in ionic strength. From the qualitative point of view, this conclusion has been shown to be valid also by Cassagne[8]. Very weak acids, *e.g.*, glycocoll, which can be salified by zinc oxide but not by ammonia, have a distinct heat sensitizing action on cream from latex degraded by trypsin, whereas they have no such action, even when in high concentrations, on normal latex.

Although the study of the heat sensitizing effect has been carried out chiefly on latex degraded by powdered pancreas, there seems to be no reason for not assuming the same mechanism when degradation has been brought about by natural aging or by thermal treatment. However, the method of degradation does affect the final properties of a latex, since the effects produced are not identical in the three cases.

Natural degradation takes place slowly and is the mildest; it is a result of hydrolysis by ammonia of the stabilizing substances, proteins, lipides, and other components, with formation of smaller molecules, which are in part desorbed.

Thermal degradation resembles natural degradation in the results obtained; in both cases the latex becomes heat sensitive and can be preserved for a long time with zinc oxide.

In biochemical degradation the action of trypsin is concerned more specifically with the proteins; however, in practice other diastases are associated with trypsin so that the degradation is not limited to simple hydrolysis of proteins.

These different modes of degradation involve both qualitative and quantitative differences, not only in the composition of the adsorbed layer but also in the composition of the serum. At each stage of degradation of a protein substance, a CO_2H group is formed, and the more advanced the degradation, the more CO_2H groups in the products, and consequently the smaller the molecules. The mode of degradation and its degree both influence the nature of the acids formed and their concentration in the serum.

The differences in two latices degraded by different methods can be explained on the assumption that scission of the protein chains is more profound in one case than in the other, or by the degradation proceeding toward acidic products of differing natures. However, this deduction still remains to be verified, and this was one of the objectives of Cassagne[8] in his study of the part played by complex zinc ammonium salts.

With respect to heat, its function in the heat sensitization of latex is to increase the rate of coagulation by three effects: (1) it increases the amount of coagulating agent by promoting solution of the zinc oxide; (2) it accelerates the dissociation of zinc-ammonium salts, with liberation of positive ions, which neutralize the negative charge on the rubber particles, and (3) it increases Brownian motion.

STABILIZATION OF TRYPSINATED LATEX

When the problem of the mechanism of the action of trypsin was attacked merely on an empirical basis, progress was insignificant; when the stability was improved, the heat sensitivity disappeared or at best became very low. Under these conditions it seemed difficult to effect a satisfactory compromise between these two characteristics as is obvious from a consideration of the processes which take place. On the contrary, several means of increasing the

stability after digestion are available. The first three to be enumerated are aimed at decreasing the ionic strength of the latex by elimination of part of the acidic substances in the serum, whereas the latter can still act directly on the dispersed phase of the latex.

(1) *Dilution and creaming.*—The serum can be partially removed by dilution, followed by concentration by creaming, but this operation is impracticable industrially.

(2) *Displacement by sodium hydroxide.*—Instead of eliminating a part of the serum, it is simpler to displace part of the ammonium salts by adding a small percentage of sodium hydroxide to the latex, which results in the transformation of a part of the ammonium salts into sodium salts:

$$RCO_2NH_4 + NaOH \rightarrow RCO_2Na + NH_4OH.$$

These sodium salts are without action on the zinc oxide and, in such small amounts, do not have any bad effect on subsequent operations. This method (the potassium hydroxide index) has already been used by Jordan[9] to eliminate ammonium salts which tend to thicken or to decrease the stability of latex in the presence of zinc oxide. However, in the problem concerned in the present work, the quantity of sodium hydroxide to be added to latex should be such that a sufficient quantity of ammonium salts is still present to maintain the heat sensitivity of the latex.

For example, the addition of 30 cc. of a 4 per cent (normal) sodium hydroxide solution to one liter of trypsinated latex gives a treated latex, which if it contains zinc oxide, can be stored for one month instead of for only two days without its heat sensitivity at 70° C decreasing appreciably. It should be added that partial displacement of the ammonium salts by sodium salts represents a selective reaction associated with the dissociation constants of the salts. The ammonium salts formed by proteolytic degradation are constituted of a complex mixture of organic acids whose ionization gradient extends through a more or less broad range, according to the conditions of degradation. A small quantity of sodium hydroxide displaces preferentially the salts of relatively strong acids, *i.e.*, those which are most harmful to good preservation of the latex, and leaves unaffected salts of weaker acids, in whose presence the heat sensitivity is maintained.

(3) *Displacement by sodium carbonate.*—The advantage of sodium carbonate is that an excess does not destroy the heat sensitivity; however, an excess is not to be recommended because of the danger of its exuding from the coagulum. Two arbitrary conditions present themselves. If the acid of the ammonium salt is stronger than carbonic acid, the reaction:

$$2RCO_2NH_2 + Na_2CO_3 \rightarrow 2RCO_2Na + (NH_4)_2CO_3$$

with formation of ammonium carbonate and the salt of the weak acid takes place. This is a condition favorable to the preservation of sensitized latex mixtures. Even when the transformation is complete, *i.e.*, with an excess of sodium carbonate, the ammonium carbonate which is formed is still capable of maintaining the heat sensitivity. On the contrary, when the acid of the ammonium salt is weaker than carbonic acid, the sodium carbonate remains practically unattacked.

In brief, the action of sodium carbonate is limited merely to destroying the harmful ammonium salts and replacing them with ammonium carbonate.

However, from a practical standpoint, sodium carbonate is less effective than sodium hydroxide. With 2.5 grams of anhydrous sodium carbonate per liter of latex, the sensitized mixture remains stable for a little more than a week.

(4) *Use of a nonionic soap.*—Certain stabilizing agents such as Igepon stabilize trypsinated latex by suppressing its heat sensitivity; other agents such as alkaline oleates have no effect on the heat sensitivity, yet prolong to no significant extent the time that the latex is stable.

On the other hand, satisfactory stabilization can be effected by means of a small amount of a nonionic soap[10], such as Vulcastab-LW or Emulphor-O; 0.25 per cent of this product (based on the latex) preserves a sensitized latex mixture for several weeks, without decreasing notably its heat sensitivity at 70° C (see Table 5). On a practical scale, this process has proved to be the most convenient one for preserving latex mixtures for a long time and thereby making it possible to utilize them for the manufacture of dipped goods.

TABLE 5

ACTION OF VULCASTAB-LW ON LATEX TREATED WITH 0.1 PER CENT OF POWDERED HOG PANCREAS

Determination	Without Vulcastab-LW	With 0.25 per cent Vulcastab-LW
Time of coagulation at 70° C	1 minute	1.5 minutes
Time of preservation at 18° C	2 days	More than 1 month

CONCLUSIONS

The present investigation shows that the heat sensitizing effect of powdered hog pancreas on degraded latex depends on a different principle from that of other methods, since it involves the mutual effect of two actions, a decrease in stability of the rubber-phase and an increase in ionic strength of the serum. For a given small increase in ionic strength, the greater the degradation of the stabilizing substances, the greater is the tendency toward coagulation. This makes it possible in practice to dispense with washing the coagulum. Since, in addition, it is possible to preserve heat sensitized mixtures for several weeks, it is obvious that this process meets most of the requirements for the manufacture of molded goods directly from latex.

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NATURAL, THERMAL, AND BIOCHEMICAL DEGRADATION OF AMMONIATED HEVEA LATEX TO GIVE HEAT SENSITIVITY*

FRANCIS LEPETIT

FRENCH RUBBER INSTITUTE, 43 RUE SCHEFFER, PARIS, FRANCE

INTRODUCTION

The development and importance in the latex industry of heat-sensitized mixtures are especially notable in processes which involve molding.

Nevertheless, heat sensitivity is a characteristic which has been made the object of relatively few scientific studies; hence it seemed interesting to undertake its investigation, limiting it, however, to the problem of Hevea latex.

Sensitized mixtures usually make use of delayed-action coagulating agents, which produce a gel of regular structure which easily takes the form of the mold into which latex has been poured. The agents are compounds capable of giving at ordinary temperature, or more rapidly by heating, either acid ions, as in the case of sodium silicofluoride[1] and of the mixture of aldehyde and ammonium persulfate[2], or positive ions as in the case of di- or trivalent oxides of metals in the presence of an ammonium salt of a strong acid[3], oxide or carbonate of zinc in the presence of an ammonium salt[4], magnesium salts of sulfonic and carboxylic acids, quinoline sulfate, alum[5], triethanolamine hydrochloride and ammonium oleate[6], isoamyl acetate[7], diphenylguanidine[8], and mercaptobenzimidazole[9], in the presence of zinc oxide.

Among these sensitizing agents, particular mention should be made of those of the Kaysam process[4], that is to say, ammonium salts (chloride, nitrate, acetate), which react in the presence of zinc oxide or carbonate serving as activator for curing. Van Neederveen and Houwink[10] have shown that gelling is caused under these conditions by the formation of positively charged zinc-ammonium complex divalent ions.

Several criticisms have been levelled at the Kaysam process, the majority of which fall on the use of an ammonium salt as sensitizing agent. The main criticisms are that, at ordinary temperature, the sensitizing agent begins to work, first by thickening the latex and then by causing it to gell, with the result that sensitized mixtures cannot be preserved for more than a few hours, and this compels their preparation in small quantities and their utilization within a restricted space of time. Thickening at ordinary temperature may retard the escaping of air bubbles from, and hinder flowing in, the mold.

Secondly, to avoid undesirable aging or the appearance of a bloom on the surface of the manufactured product, the ammonium salt must be eliminated by washing the coagulum after removal from the mold in warm water, a long process requiring several hours.

Thirdly, as washing is not effective except for relatively thin articles, this process hardly makes possible the manufacture of thick articles.

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In addition, the use of latex preserved with potash is recommended for the Kaysam process, whereas ammoniated latex would present advantages as it is more readily available than potash latex. During the drying of the gel, the ammonia evaporates away easily, whereas the use of latex preserved with potash makes the washing of the gel absolutely indispensable to remove the fixed alkali and the soaps that it contains. Finally the presence in latex preserved with potash of protective colloids slows the drying[11] and, after curing, the objects are more plastic and more easily oxidizable[12] than those obtained from ammoniated latex.

These difficulties are apparently eliminated by replacing the ammonium salt by nitroparaffins[13] usable with an ammoniated latex, but the industrial supply of these compounds is still uncertain.

The author has made every effort to eliminate the addition of an ammonium salt and to sensitize the latex, not by acting on the ionic strength of the serum as in the Kaysam process, but by diminishing the charge of the rubber globules. From the theory of Debye and Hückel applied to suspensoids[14], it is known that the coagulation of a colloidal emulsion such as latex is determined by the value of its electrokinetic potential ψ given by the formula:

$$\psi = \frac{E}{Da} \cdot \frac{1}{1 + aA\sqrt{\mu}}$$

in which:

ψ = electrokinetic potential
E = charge on rubber globule
D = dielectric constant of the dispersing medium
a = radius of the globule
A = constant
μ = ionic strength of the dispersing medium represented by

$$\mu = \Sigma n_i z^2$$

where n_i is the number of ions of type i and of valence z_i per unit of volume.

The tendency towards coagulation increases when ψ decreases, that is, when the ionic strength μ of the serum increases or when the charge E of the rubber globule diminishes. Several means have been discovered to lower that charge by degrading the stabilizing materials of latex, and to make the latter coagulable under the influence of a slight increase in ionic strength, that is, in the presence of a small amount of ammonium salts.

In the present paper, the author discusses the various cases of degradation of ammoniated latex, whether that degradation takes place naturally, or whether it is brought about by thermal or biochemical means.

NATURAL DEGRADATION OF LATEX

The tests were carried out on old latex. In the course of its preservation, ammoniated latex undergoes certain changes[15] which are due to the action of ammonia, which tends to hydrolize the proteins and to cause the products of deterioration to go into the aqueous phase, in which they combine with the free alkali to form ammonium salts. This causes a decrease in the free ammonia content, an increase of ammonium salts, and a change in the stability of the latex during the first months of storage.

Only a few observations have been recorded of the characteristics of an ammoniated latex preserved for more than six years. The author began his study of such a latex in 1944, since hostilities prevented a supply of new latex.

This latex contained 57 per cent of solid substances and 0.8 per cent of NH_3; although free from clots, it was rather unstable and coagulated easily when rubbed between the fingers.

From a practical point of view, its most interesting characteristic lay in the fact that it became sensitive to heat[16] in the presence of zinc oxide alone, without the addition of an ammonium salt. By adding 0.25 cc. of a 33 per cent dispersion of zinc oxide (3 per cent of zinc oxide on the rubber) to 5 grams of latex, a mixture was obtained which coagulated in two minutes at 70° C, with the formation of a gel having all the requisite qualities for obtaining molded articles, namely, coherence and firmness at the moment of removal from the mold, elimination of washing, and even contraction while drying. Moreover, the sensitized mixture remained stable for several weeks at ordinary temperature, washing was unnecessary, and the ammonia evaporated away during the drying of the coagulum.

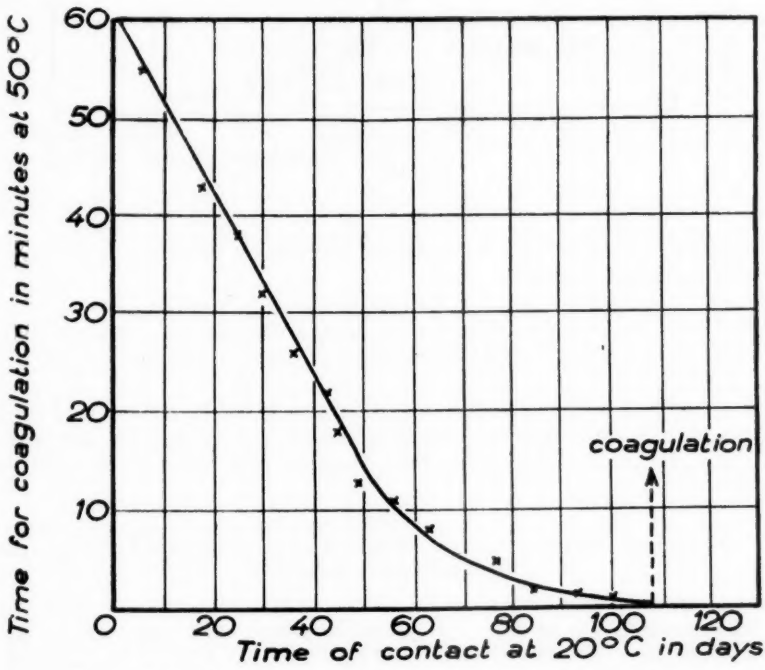

FIG. 1.—Influence of preservation time of mixture on heat sensitivity at 50° C.

Thus, under certain conditions, the use of ammoniated latex eliminates the inconveniences of the Kaysam process.

Length of preservation of old latex in the presence of zinc oxide.—During the period of preservation, the zinc oxide reacts progressively with the ammonia and the ammonium salts of the latex, freeing positive ions. The mixture becomes more and more sensitive to heat, then it thickens, and coagulates after three months at a temperature of 15°–20° C (Figure 1). If the room temperature is higher, the mixture reacts more quickly, and in summer the duration of preservation is about two months, which, practically speaking, is still fully sufficient.

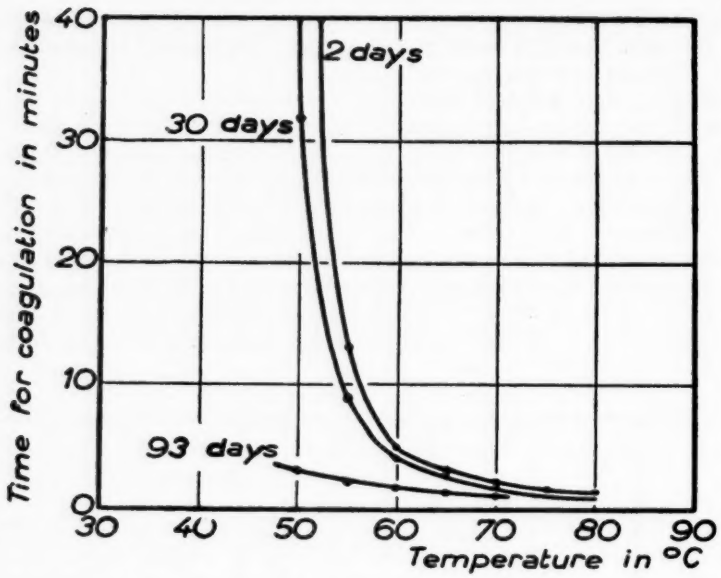

FIG. 2.—Influence of temperature on rate of coagulation for preservation time of 2, 30 or 93 days.

Coagulation temperature.—The rate of coagulation increases rapidly as the temperature rises (Figure 2).

At 70° C, the difference which may exist between the sensitivities of several mixtures is no longer discernible, for the rate of coagulation is too quick; that is why it is sometimes preferable to measure heat sensitivity at 50° rather than at 70° C.

From an examination of Figure 2, it is observed that for a sensitized mixture to be stable at room temperature in the presence of zinc oxide, the temperature at which it coagulates (2 to 5 minutes) must be very different from ordinary temperature (about 50° C).

TABLE 1

INFLUENCE OF THE QUANTITY OF ZINC OXIDE ON HEAT SENSITIVITY (AFTER 10 DAYS CONTACT)

ZnO (per cent on dry rubber)		0.25	0.50	1	3	5	10
Coagulation time in minutes	at 50° C	>60	>60	50	60	55	60
	at 70° C	>60	13	2	2	2	2

Quantity of zinc oxide.—Table 1 shows that doses of 0.25 and 0.50 per cent (on the dry rubber) of zinc oxide do not cause the latex to become sensitive to heat at 50° C; however, at 70° C, sensitivity begins to appear with 0.5 per cent.

Sensitivity reaches a maximum with 1 per cent of zinc oxide and, in this case, the mixture remains stable for two months at ordinary temperature.

A larger quantity would have tended to decrease slightly the sensitivity, and mixtures remain stable three months; this effect is due to dilution and to the presence of a greater quantity of dispersing agent which accompanies the zinc oxide.

In practice, 3 per cent is the most favorable, the zinc oxide also activating the cure.

Degree of purity of zinc oxide or zinc carbonate.—Van Nederveen and Houwink[11] observed that a mixture of ammoniated latex and zinc carbonate would coagulate quickly at ordinary temperature (in 30 minutes). Since, in our case, the stability of a sensitized mixture extended three months, we examined the influence of products of different origins: the unfavorable result obtained by the above-mentioned authors may be due to impurities in the zinc carbonate.

Table 2 indicates the heat sensitivity produced by five oxides and three carbonates of zinc added to the same latex (3 per cent in proportion to rubber) in the form of aqueous dispersions.

TABLE 2

SENSITIZATION OF AMMONIATED LATEX BY DIFFERENT OXIDES AND CARBONATES OF ZINC

Time of preservation of sensitized mixture	Coagulation time in minutes at 50° C							
	Zinc oxide				$Zn(OH)_2$ precipitated	Zinc carbonate		
	1	2	3	active		pure	techn.	coml.
1 day	65	100	85	gelled at room temp.	gelled at room temp.	160	>160	gelled at room temp.
10 days	50	90	60	—	—	135	100	—

The zinc oxides 1, 2 and 3 are commercial products, 1 being used. All three impart to the latex about the same sensitivity, and a time of preservation exceeding two months.

Freshly precipitated zinc hydroxide was prepared by adding a definite amount of ammonia to a solution of zinc sulfate; the gelatinous precipitate was then filtered and washed with warm water. With this precipitate, we made a new suspension in water before mixing with the latex. Commercial carbonate of zinc, in the final column of Table 2, would correspond to the formula, $ZnCO_3 \cdot ZnO \cdot H_2O$, and would, therefore, be a basic zinc carbonate.

Active zinc oxide, precipitated zinc hydroxide, and the commercial carbonate of zinc quickly thicken the latex and coagulate it after one day of contact at ordinary temperature. We have sought to discover whether the cause of this coagulation is not due to the presence of impurities which produce an excess of positive ions in the latex.

The products were, therefore, extracted with boiling water and the aqueous extracts were analyzed (Table 3).

The quantities of aqueous extracts and sulfate ions are important in the case of active zinc oxide and of precipitated zinc hydroxide, both gelling latex quickly at room temperature.

TABLE 3

CHEMICAL COMPOSITION OF AQUEOUS EXTRACTS RESULTING FROM WASHING ZINC OXIDES AND CARBONATES

Constituents	ZnO 3	ZnO active	$Zn(OH)_2$ precipitated	$ZnCO_3$ pure	$ZnCO_3$ coml.
Per cent dry aqueous extract	0.22	5.36	4.63	2.11	0.71
SO_4^{--}	0.055	3.12	3.16	Traces	0.50
Cl^-	0.024	0.023	None	0.021	0.012
Zn^{++}	Traces	Slight traces	1.40	Slight traces	Slight traces

In addition, precipitated zinc hydroxide contains an appreciable amount of zinc ions, which suggests the presence of basic sulfate adsorbed during precipitation[17]. As for commercial carbonate of zinc, its coagulating effect can hardly rest on the existence of impurities, since its aqueous extract is small. We are, therefore, dealing with a basic zinc carbonate, which is soluble in ammonia[18], and we have verified it experimentally. Rapid coagulation of latex at room temperature results from an excess of zinc-ammonium ions.

After their separation with boiling water, the powders were added to the latex in the form of aqueous dispersions (Table 4).

Even after washing with boiling water, active zinc oxide and precipitated zinc hydroxide gell the unheated latex; this effect is due to the adsorbing properties of these products, which hold the impurities energetically and which still show, after extraction, the reaction of sulfate ions. Washing with ammonia would perhaps eliminate the impurities more easily.

After the hot water treatment, the zinc carbonate behaves as an ordinary product; it is insoluble in ammonia and sensitizes the latex in a normal manner. Its treatment must, in fact, have modified its chemical structure and changed its basic form into a mixture of ordinary zinc oxide and carbonate. To sum up, it is important to avoid the presence of ionizable impurities or of basic zinc salts which, by increasing the quantity of complex zinc-ammonium ions, would lead to the rapid gelling of the sensitized mixture.

TABLE 4

SENSITIZATION OF AMMONIATED LATEX BY WASHED POWDERS

	Coagulation time in minutes at 50° C				
Time of contact	ZnO 3 washed	ZnO active washed	$Zn(OH)_2$ precipitated washed	$ZnCO_3$ pure washed	$ZnCO_3$ commercial washed
1 day	55	gelled when cold	2	50	45
10 days	50	—	gelled when cold	30	30

The ammonia content of latex.—The formation of complex zinc-ammonium ions necessitates the presence of zinc oxide, of free ammonia and of an ammonium salt.

In the latex, the free ammonia has opposite effects; on the one hand, a coagulating effect favoring the formation of complex ions; and on the other hand, a stabilizing effect due to the excess of ammonia above the amount required to give the complex, an excess which increases the negative charge of the rubber globules.

It would, therefore, be expected that the heat sensitivity would be at a maximum for a certain concentration of ammonia, and that is what has been verified experimentally.

For small contents of ammonia (0.1 to 0.2 per cent), the heat sensitivity is nil or very slight; coagulation occurs after a period of heating, much more because of the instability of the latex than because of the presence of zinc oxide. For higher concentrations, heat sensitivity increases and reaches its maximum at about 0.35 per cent of ammonia. Above that content it decreases slowly, becoming small for 3 per cent of ammonia.

In practice, a variation of 0.2 per cent in the ammonia content of the latex has hardly any effect on the time of coagulation.

Replacement of zinc oxide.—An examination has been made to determine whether the zinc oxide could be replaced by other compounds capable of giving positive ions.

Cadmium oxide, magnesia, lime, carbonates of cadmium, of magnesium and of calcium have been added to the latex in the form of dispersions to give 3 grams of ingredient for 100 grams of dry rubber.

Lime and magnesia bring about (almost immediately) partial coagulation of latex due probably to their adsorbing properties. Cadmium oxide coagulated the latex at first after two days of contact, but analysis revealed an impure product containing 4.45 per cent of SO_4 ions; after purification its action was comparable to that of zinc oxide. Carbonates of cadmium, of magnesium and of calcium do not sensitize latex; however, the addition of an ammonium salt (0.5 cc. of 4*N* ammonium sulfate to 5 grams of mixture) produces coagulation at 70° C in 5 minutes.

As calcium and magnesium do not form complex ions with ammonia, gelling is caused by the formation of an ionizable metallic salt. Thus, for example, magnesium carbonate dissolves into a solution of ammonium sulfate on heating:

$$MgCO_3 + (NH_4)_2SO_4 \rightarrow MgSO_4 + (NH_4)_2CO_3$$

and the magnesium sulfate which results is able to coagulate the latex.

Nature of the latex.—Tests of heat sensitivity in the presence of 3 per cent of zinc oxide were made on some latices preserved for several years and consequently not very stable.

A latex, concentrated to 59 per cent by centrifuge and preserved with ammonia and which had been kept in an iron can which had given it a grayish tint due to iron sulfide, was more sensitive to zinc oxide than ordinary old latex; after a week at ordinary temperature, the mixture thickened greatly and was useless. It is probable that a newer and more stable latex would have kept longer with zinc oxide.

A latex concentrated by heating and preserved by potash and soaps and mixed with zinc oxide becomes heat sensitive after ten days and coagulates after about twenty days.

Recent ammoniated latex.—The tests following were carried out on a recent ammoniated latex from the Cameroons. It was concentrated by creaming with methyl cellulose. This latex contained 59.5 per cent of dry material and 0.67 per cent of NH_3, and appeared to the touch much more stable than the old latex. As expected, it was not heat-sensitized by zinc oxide.

THERMAL DEGRADATION

Thus, the problem was to reproduce artificially in new ammoniated latex the transformations which had occurred in the old latex so as to make it coagulable by heat without adding an ammonium salt to it.

We could not consider using natural degradation, because it was much too slow; thus after fifteen months of preservation, the ammoniated latex was not heat sensitive after the addition of zinc oxide, although its free ammonia content had passed from 0.67 to 0.52 per cent.

It was a question, then, of speeding up this natural degradation, and heat was tried, as it increases the speed of all reactions.

The first trial consisted of heating the latex in a sealed tube to 70° C (in an oven) for twelve days, but gave a negative result.

On the other hand, heating in a sealed tube for from two to three hours in an autoclave at 143° C gave heat sensitivity on adding zinc oxide. If the

temperature of degradation was too high or if heating at 143° C was prolonged beyond four hours, the latex coagulated during the treatment.

New latex degraded by heating remains stable for two and one-half months in the presence of zinc oxide at ordinary temperature (Table 5), a common characteristic of old latex.

TABLE 5

HEAT SENSITIVITY OF A HEAT-DEGRADED AMMONIATED LATEX
(2 HOURS IN AN AUTOCLAVE AT 143° C)

Time of preservation in days with 3 per cent of zinc oxide	0	1	4	45	75
Time of coagulation in minutes at 70° C	20	10	5	1	gelled at room temperature

Consequently, thermal degradation probably brings about transformations analogous to those which result from natural aging. However, it presents certain inconveniences. First, heating latex in an autoclave is not a practical operation; secondly, after drying and curing, the unwashed coagulum obtained from the thermally degraded latex is smooth and free from exudations, but it presents a superficial brown color; this darkening, which begins at the time of drying, is due to the oxidation by the air of the products of degradation; and thirdly, although the aging of the rubber obtained is satisfactory, its tensile strength remains less by about 40 kg. per sq. cm. than that of an untreated mixture, for the rubber also undergoes a certain degradation due to the effect of the heat.

It was, therefore, thought that biochemical degradation of the latex with the aid of proteolytic ferments would be much more specific for proteins and more easily applied.

It must be noted that the removal of proteins from latex to obtain a purified rubber with the best electrical properties is effected by the hydrolyzing action of alkalies and ferments[19], the deterioration of proteins being as nearly complete as possible. But so far as heat sensitivity is concerned, latex need only be partially degraded to give it a minimum of stability.

BIOCHEMICAL DEGRADATION

Among the most widely used proteolytic diastases, pepsin is efficient in an acid medium, papain in a neutral one, and trypsin requires an alkaline medium[20]; the latter was therefore selected to degrade the proteins of ammoniated latex. As a source of trypsin, we made use of commercial powdered hog pancreas, which is clear in color and results from the rapid vacuum-drying at low temperature of defatted hog pancreas (20 to 25 grams of powder are obtained per pancreas). It keeps its properties indefinitely provided that it is preserved from dampness. It was added to the latex in the form of a 10 per cent aqueous suspension, prepared at the time of use; trypsin being soluble in water, the albuminous matter remains suspended and can be separated by centrifuging. However, the results are practically identical whether the raw suspension or a centrifuged suspension is used.

The influence of different factors was reviewed in the following manner: to new ammoniated latex, containing 59.5 per cent of dry material and 0.67 per cent of ammonia, was added the desired amount of an aqueous suspension of 10 per cent powdered hog pancreas, this suspension being freshly prepared.

After digestion, 10 grams of degraded latex were mixed with zinc oxide (3 per cent on the rubber), then divided into two parts, one being used to

determine the time of coagulation at 50° C, the other to measure the time during which the mixture remains stable at ordinary temperature.

Quantity of enzyme.—From Table 6 it is seen that the greater the enzyme content of the latex the greater the heat sensitivity. Moreover, when heat sensitivity was obtained, coagulation of the mixture occurred quickly at room temperature.

TABLE 6

INFLUENCE OF QUANTITY OF ENZYME ON SENSITIVITY OF AMMONIATED LATEX AFTER 5 DAYS OF DIGESTION

Enzyme per cent of latex		0.025	0.05	0.1	0.2	0.5
Coagulation time	at 50° C in minutes	>30	30	13	4	1
	at 18° C in hours	>24	15	10	3	1

Later, 0.1 and 0.2 per cent of enzyme which moderately degraded the latex in a short time were used. The 0.025 per cent content is insufficient to sensitize the latex rapidly after addition of zinc oxide, but sensitization occurs after two or three days of contact with zinc oxide. Then the mixture coagulates at room temperature after one week.

As small a quantity of enzyme as 0.01 per cent produces spontaneous coagulation in the absence of zinc oxide after about twenty days of digestion, without the appearance of sensitivity to heat when zinc oxide is added.

Time of digestion.—The larger the amount of enzyme, the more quickly heat sensitivity appears as a function of digestion time (see Table 7).

TABLE 7

INFLUENCE OF DIGESTION TIME ON HEAT SENSITIVITY AT 50° C

Digestion time in days at 18° C		1	2	3	4	5	7	10	15	20
Coagulation time in minutes at 50° C	0.1 per cent of enzyme	>30	>30	30	18	13	8	5.75	4	3.25
	0.2 per cent of enzyme	>30	10	4.25	3.25	2.75	2.25	2	2	2

Treated with 0.2 per cent of enzyme, the latex becomes heat sensitive after two days of digestion, and degradation goes practically no further after five to seven days (Table 7).

Digestion temperature.—When the digestion is brought about by heat, degradation is at first more rapid than by digestion at 18° C, but it remains more incomplete, with the result that the latex is less sensitive in the presence of zinc oxide (Table 8). This effect results from the acceleration by heating of the biochemical degradation of proteins. But it decreases the activity of the enzyme. An aqueous solution of pancreas powder held at 42° C for 20 hours loses its proteolytic properties and has no effect on the latex.

TABLE 8

INFLUENCE OF TEMPERATURE OF DIGESTION ON HEAT SENSITIVITY OF A LATEX TREATED WITH 0.2 PER CENT OF ENZYME FOR 5 DAYS

Digestion temperature		18° C	30° C	42° C
Coagulation time	at 50° C in minutes	4	15	20
	at 18° C	3 hours	2 days	2 days

Heat is thus not favorable to a good digestion in the case of trypsin, but it can be applied to stop the enzymatic action; fifteen minutes heating at 70° C causes the action of the enzyme to cease.

The presence of a very small quantity of enzyme (about 0.01 per cent) and digestion at 42° C are favorable to the spontaneous coagulation, which happens when the degradation remains incomplete. In these conditions, coagulation occurs after about six days of digestion, without any heat sensitivity appearing when zinc oxide is added. This result will be explained in another communication.

Nature of the latex.—Instead of degrading concentrated latex, unconcentrated latex may be degraded before creaming it. Ordinary latex (35 per cent dry rubber content) treated with 0.2 per cent of hog pancreas powder and digested for five days is less heat sensitive (13 minutes at 50° C) than concentreated latex (59 per cent dry rubber content) degraded under the same conditions (2.75 minutes at 50° C), the greater dilution of the first decreasing the probability of contact between the rubber globules. But after creaming of the degraded 35 per cent latex, heat sensitivity is equivalent to that of latex creamed first and then degraded.

To determine whether old latex was capable of being degraded still further, it was treated with 0.2 per cent of enzyme and digested for five days. Its heat sensitivity was increased as a result (4 minutes at 50° C instead of 60 as at first) and the stability of the sensitized mixture in the presence of zinc oxide decreased from two months to 2 days. The enzyme action is thus effective on old latex; the natural changes during six years storage are only partial.

Nature of the pancreas powder.—The above tests were carried out with pancreas powder from which the fats had been removed. Whole pancreas powder acts more slowly; the fats which it contains doubtless have a tendency to stabilize the latex, but in practice the differences are negligible.

Replacement of trypsin by other diastases

Action of papain.—Papain is a vegetable proteolytic diastase whose efficiency is at a maximum at pH 7 and at about 70° C. Under other conditions its action is delayed.

Papain is contained in the sap of *Carica papaya*, a wild plant abundant in the colonies. Baker[21] used this enzyme, and increased its action by a small quantity of potassium cyanide to deproteinize ordinary ammoniated latex.

Creamed latex was treated with 0.5 per cent of raw papain powder and left to digest at 60° C (in an oven) in the absence of cyanide. After two days digestion, heat sensitivity appeared from the moment when zinc oxide was added (coagulation in 2 minutes at 70° C and in 3 hours at ordinary temperature).

After four days digestion, spontaneous and partial coagulation of the latex occurred.

Action of pepsin.—Baker[21] has shown that the action of this diastase is very weak in the removal of proteins from ammoniated latex.

Action of batinase.—This product possesses a proteolytic activity at pH 6–7 and at about 55° C. Applied to latex its efficiency is slight and the heat sensitivity remains small.

Action of microbes.—Several microbes are capable of proteolytic activity by means of the diastases which they secrete.

In new latex sown with different cultures of *bacillus subtilis, mycoides,* or *licheniformis,* no sign of fermentation appeared after three days at 30° C.

It is possible that the spontaneous fermentation of fresh latex, which

develops naturally before preservation by ammonia or which one may assist by the addition of microbic muds[22], deteriorates it sufficiently to make the latex heat-sensitive, in this case ammonia and zinc oxide being added later.

APPLICATIONS

The premature coagulation which occurs in sensitized mixtures based on trypsin-degraded latex has been applied to molding at ordinary temperature.

Ammoniated latex (58–60 per cent dry rubber content and 0.6 per cent ammonia) is treated with 0.2 per cent of hog pancreas powder in the form of a 10 per cent aqueous suspension. After four or five days of digestion at room temperature, the latex is degraded, but is still sufficiently stable to allow its normal preservation, even in presence of vulcanization ingredients, zinc oxide, of course, excepted. The latter is added at the time of use (3 per cent of zinc oxide on the rubber) and the mixture is cast into the mold. Gelification takes place after two or three hours or less, according to the room temperature, and this makes the processing particularly convenient for tropical countries.

This process offers numerous advantages, among which it is fitting to point out first that the elimination of heating offers economy and simplification of apparatus: this advantage is especially appreciable in the manufacture of articles requiring cumbrous molds. Secondly, the coagulum may be joined to itself whenever the manufacture of an article requires an assembly from separately molded pieces; and thirdly, it is possible to develop the use of molds of inexpensive materials which by their weight, fragility and poor heat conductivity are applicable with difficulty to the manufacture of articles by other processes.

A great number of manufacturing processes can be revised on the above lines, but the method is protected by a S.A.I.F.C. patent.

APPENDIX

DETERMINATION OF HEAT SENSITIVITY

Five grams of latex mixture to be examined are poured into a pyrex test-tube (16 mm. diameter) containing a stirring rod bent at the lower end to a hook which serves to extract the coagulum. The tube is placed in a water thermostat (Figure 3) and the time needed for the coagulation of the mixture

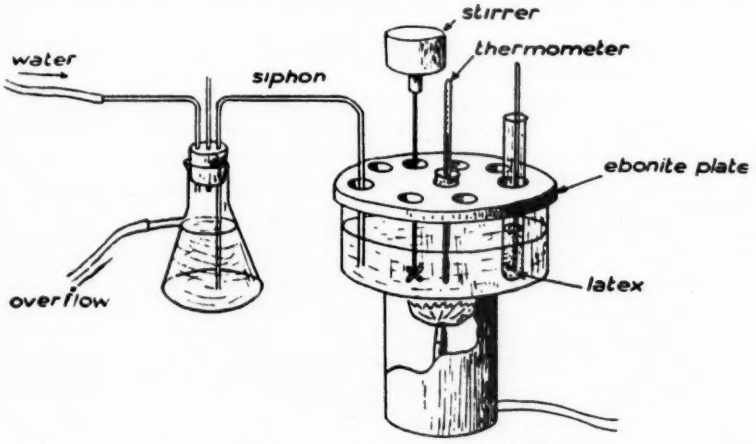

FIG. 3.—Device for determination of heat sensitivity.

is measured. This is determined by stirring the mixture with the glass rod. The mixture first thickens and finally coagulates completely, when the coagulum may be completely removed on the hook of the rod. The coagulum may be retained for further examination or vulcanization.

This determination is obviously rather empirical, for the time for gelling is subject to possible error, due in particular to the thickness of the wall of the test-tube, to the thickness of the mixture to be coagulated, to variations of temperature of the thermostat, and to the time before the contents of the tube are definitely at the temperature of the thermostat. It is important, therefore, in order to obtain reproducible and comparable results, to operate always under the same conditions.

The formula of the mixture which was used is as follows:

Rubber	100 parts by weight
Sulfur	1 part by weight
Zinc oxide	3 parts by weight
Zinc diethyldithiocarbamate	1 part by weight

The ingredients were added to the latex in the form of aqueous dispersions prepared in a ball-mill with the help of dispergine C.B. (Kuhlmann). The coagulum can be vulcanized in 1 hour in an oven at 100° C.

SUMMARY

In most heat sensitizing processes ammonium salts are added to the latex, with consequent complications in manufacturing operations. A method is described which eliminates the use of ammonium salts and in which heat sensitivity of ammoniated latex in the presence of zinc oxide is obtained by natural aging, by heat treatment, or by biochemical methods. With natural aging or heat treatment, the sensitized mixture is stable at ordinary temperature provided the zinc oxide (or carbonate) is free from ionizable impurities.

Biochemical degradation of the latex is readily obtained by adding trypsin. It produces sensitized mixtures which gel quickly and satisfactorily at ordinary temperature, and which are suitable for the manufacture of articles, even of great thickness in cold molds, the resulting coagulum needing no washing on removal from the mold.

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MICROGEL, A NEW MACROMOLECULE. RELATION TO SOL AND GEL AS STRUCTURAL ELEMENTS OF SYNTHETIC RUBBER *

W. O. BAKER

BELL TELEPHONE LABORATORIES, MURRAY HILL, N. J.

In connection with the rubber crisis of the war, useful fundamental controls and improvements of quality of synthetic rubber which would fit in with current engineering were urgently needed. Variations in the solubility of butadiene polymers and copolymers had been noted by many rubber researchers seemingly to reflect important and controllable variables in the polymerization process, such as "modification" and degree of conversion. Solubility also was thought by some workers to bear on processability. Agreement was neither definite nor general on these phenomena. Solubility behavior and gel fraction had been casually observed for thirty years in natural and synthetic rubbers studied in Europe. No record of engineering application was found.

After the organization of the polymer research program in the Office of the Rubber Director, more intensive examination of the significance of sol-gel in controlling the uniformity of GR-S was begun.

A proposal new to polymer technology was made, *viz.*, that the gel fraction of synthetic rubber comprised a characteristic structure in the raw polymer which affected the physical properties and quality (as in tire performance) of the final vulcanizate.

This idea is to be distinguished from those of Spence and Ferry[1]. Here, extensive vulcanization of natural rubber by air, sulfur, and other "catalysts" was measured by solubility and swelling volume in benzene. The results were then interpreted in connection with the stress-strain properties of the given rubber samples after compounding and further vulcanization in the usual way. The conclusions on quality were, quite properly, that Hevea rubber containing gel resembled in many ways a good vulcanized stock or at least fine, air-dried Para rubber, and yielded faster curing stocks. Similar results on the effect of gel in Hevea had been found by Smith and Holt[2] and Smith and Saylor[3].

However, the present work concerns the more local structure of the gels of emulsion polymers. These are, indeed, units causing certain intrinsic properties of the rubber other than the degree of cure.

Likewise, it was indicated that certain elements of processing, as well as the initial synthesis, could affect this structure in synthetic rubber and thereby obscure vital relations between polymerization and tire quality, as well as themselves reduce that quality.

The present report concerns the basic concepts of gel compared to sol, particularly in emulsion polymers. Other reports will describe the methods of identifying sol and gel and their significance in the synthesis and processing of

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synthetic rubber. Indeed, important applications of these concepts and techniques have already been described[4].

CHRONICLE

Thomas Graham and other early philosophers recognized the network properties of gels[5], although frequently they meant secondary valence networks, with which we are not now concerned. Nevertheless, the swelling of vulcanized rubber[6] and of a portion of raw rubber found benzene-insoluble after fifteen years of aging[7] furnished behavior that forecast the present interpretation. At an early symposium on colloids, it was said, "the jelly would tend to swell to infinity and ultimately dissolve; and since it does not do so, we must assume some opposing force, and the only possible one appears to be the elastic cohesion of the jelly, which implies some sort of connected structure"[8]. Now, taken with the contribution of Staudinger[9] in establishing the beautiful generality of macromolecules, or huge primary valence bonded units (as opposed to vague theories of cemented micelles), this provides most of the basis for interpreting the gel phase in cross-linked polymers.

There have been long argument and uncertainty, however, as to how such networks were formed chemically, as during polymerization, and thus as to why some polymers were all sols (in suitable solvents), whereas others were largely gels (in all solvents). Staudinger, with his bold thesis of primary-valence chains and networks, showed how certain organic units could lead to network gelation[10]; a similar approach was clarified and systematized by Carothers[11] and Kienle[12]. Then, specific mechanisms for gelation in polybutadiene, natural rubber, etc., with hydrogenation experiments to examine the nature of branched fragments[13] were followed by data on polyester resins and drying oils[14]. It is known now that the chemical reactivity of natural rubber often prevented earlier consistent isolation of its sol and gel components[15]. This is especially because the isoprene residue is liable predominantly to oxidative scission, in contrast, for example, to the butadiene residue, which is readily cross-linked.

Finally, a theory for a statistical interpretation of polymer gelation as infinite network formation has been developed[16]. Generalizations[17] have further affirmed the reality of the molecular network model. Likewise, recent experiments with various monomers, each of known functionality, have agreed with gelation concepts. Examples include divinyl ether[18], hydroquinone diacrylate[19], other unsaturated esters[20], and partially methylated cellulose cross-linked with oxalyl chloride[21].

On the other hand, the true solubility of essentially linear polymer molecules has been widely established following Staudinger's early concepts. A model for thermodynamic understanding of such solutions, proposed by Meyer[22] has been applied in the well-known contemporary theories[23] of high polymer solutions, whose agreement with experiment[24] is at least indicative of a basically valid idea.

This is that, above a critical temperature[25], chain molecules are infinitely miscible with some solvent whose heat of mixing with the polymer is tolerable; GR-S sol with benzene seems to be an example. However in partial solvents, or in solvent-nonsolvent mixtures, even strictly linear molecules show a solubility or phase separation which depends on molecular weight[26]. This is the old scheme for polymer fractionation. Insolubility caused in this way is not to be confused with the insolubility of networks or gel. The solubility of linear

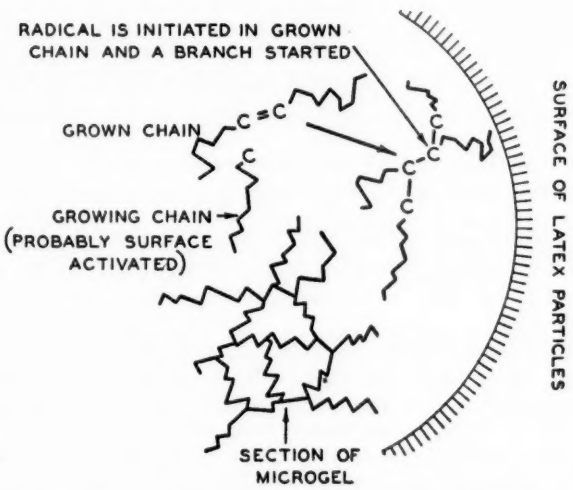
macromolecules was attributed by Brönsted[25] and Schulz[27] to a favorable potential energy state for the dissolved macromolecule contrasted to its solid state of aggregation. Previously, however, Meyer had emphasized a high entropy of mixing for the formation of polymer solutions. Schulz's theory of potential energy change on solution was especially criticized for its neglecting the predominant entropy change[28]. The recent studies noted take care of this[23], and entropy gain is probably the chief cause of dissolution of most hydrocarbon polymers[24]. However, the heat or solvation factor has also been evaluated for hydrocarbons like natural rubber[29], and conditions for dissolving polymers can now be defined.

This is the background from which the study of sol-gel in GR-S and other butadiene polymers has been proposed to reveal essentially distinct and significant, although chemically interconvertible, elements of structure.

MICROGEL

Association of sol-gel structures with quality control of GR-S first required separation of the gel phase. All the earlier considerations and experiments, surveyed above, were with gelations in which the infinite network essentially spread through the whole containing vessel, solution, or (as in vulcanization) mold. Coherent, readily separable, agglomerates of gel, from which most of the sol was extracted, were formed in phenolic resins, alkyds, vulcanized rubber, mass-polymerized Buna, etc.

Emulsion polymerization, however, sharply localizes gelation. For the reaction unit is here the latex particle (or soap-monomer aggregate preceding it). With regular GR-S, its average diameter of 1000 to 2000 Å. or volume of 0.5 to 4.5 $\times$ 10^{-15} cc. means that the largest gel network is still only of supermolecular size and weight (with M around 60 $\times$ 10^6, or only 30 times that of high molecular weight polystyrene). This unit was called microgel[30]. It can be separated only under static conditions, which lead to a particular, possibly often chemical, agglomeration. This is treated in the report on techniques.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GROWN CHAIN
GROWING CHAIN (PROBABLY SURFACE ACTIVATED)
SECTION OF MICROGEL
SURFACE OF LATEX PARTICLES

FIG. 1.—Schematic diagram of microgel formation in polybutadiene.

Whether microgel sometimes occupies a whole latex particle, or is found in particular types of latex particles, is not yet well known. It may be especially common in smaller latex particles[31]. These and related problems involve the detailed mechanism of emulsion polymerization[32]. But microgel is the form of primary reaction gel in GR-S while that coming from drying, aging, vulcanizing, etc., is macrogel[33].

Microgel is probably formed in polydienes by the reaction illustrated in Figure 1.

Evidently, such network formation is governed by accessibility and concentration of catalyst, modifier, monomers, etc. Hence, in Figure 1 the reactions shown are probably affected by surface to volume ratio, *e.g.*, latex particle size.

OBSERVATION OF MICROGEL

Contents of emulsion polymerization latex particles may be uniformly dispersed in lyophilic liquids by the vistex technique[35]. Here, a small volume of latex is dissolved in a xylene-pyridine (75:25) or similar solvent mixture.

A similar scheme of converting the polymer in latex (lyophobic system) into a solution or dispersion of the polymer (lyophilic system) on which meaningful viscosities, etc., may be run was apparently worked out in Germany[35]. However, chlorobenzene and like solvents which "extracted" but did not wholly take up the latex were used by boiling the water off, and hence some coagulation may have preceded dispersion.

With a polymer containing microgel, this dispersion would be a true solution of the sol fraction and also of the microgel particles unless they happen to be large enough to sediment spontaneously. (In the latter case, sedimentation equilibrium may come so slowly that a colloidal dispersion of the large microgel, rather than a true solution, exists.) A similar system would result if a polymer containing microgel were coagulated from the latex, and then, without any reaction with oxygen, etc., to introduce macrogel, were redispersed in a solvent, say, benzene. This redispersion could occur from agitation, and again, the system would be a true solution of polymer including microgel, or, for very large particles of microgel, a colloidal solution of microgel. This distinction between true and colloidal solution of course depends entirely on the size of the microgel.

This latter case, where a coagulum protected from oxygen is redispersed, is especially familiar in GR-S studies. Such a dispersion in benzene was made from a form of GR-S brought to 85 per cent conversion and containing 57 per cent microgel of swelling volume 35. This swelling volume (approximately the multiplication in volume of the solid, unswollen gel caused when it is in equilibrium with benzene at 25° C) denotes a density of cross-linkages[36] high enough so that the microgel particles should be fairly rigid and hold their shape when deposited from dispersion. Thus if they were deposited from a dilute dispersion, a very thin flat film of the sol fraction should contain much thicker mounds of microgel.

Accordingly, the dispersion noted above was prepared to contain 0.25 gram of polymer per 100 cc., and was spread with a special micro doctor blade on a clean glass slide so that the sol formed a film, after evaporation of benzene, about 200 to 300 Å. thick (as estimated from interference colors). The microgel particles would be expected to stick up from this thin film as thicker pieces, 500 to 5000 Å. thick (several would probably agglomerate together). To see if this occurred, the film was floated off the slide in distilled water, and pieces

were picked up on structureless silica films also about 200 Å. thick (made by vapor deposition of silica[37]. The silica bearing the thin sol film with its assumed protrusions of microgel was then put on a holder and examined in an electron microscope by C. J. Calbick of these laboratories.

A photograph typical of many specimens studied appears in Figure 2, *A*. Against an essentially structureless background (at the magnification of 21,600× shown), black particles denote thicker areas caused by semirigid microgel. Many of the particles are smaller than the average latex particles.

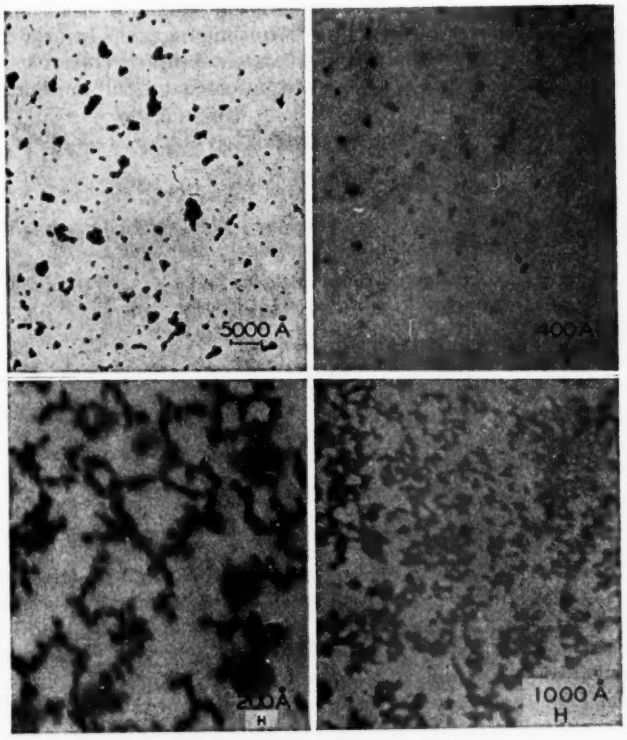

FIG. 2.—Electron micrographs of microgels.

A. Microgel from undermodified butadiene-styrene copolymer. 21,600×.
B. Polybutadiene microgel deposited from very dilute solution in cyclohexane. Patches in background are from 14% of sol present in polymer. 25,600×.
C. Polybutadiene microgel deposited from 0.1% solution in cyclohexane. Chainlike structure is probably prelude to agglomeration. 58,600×.
D. Microgel from methyl methacrylate-ethylene diacrylate emulsion polymer of 84.4% conversion, 6.8 weight % of cross-linking agent used. Individual molecules poorly resolved. 23,300×.

Several very large microgel aggregates appear. These are groups which were not broken up when the original coagulum was dispersed in benzene, or which formed when the film was deposited. In either case, they suggest definite agglomerating tendency of microgel, of importance in consideration of sedimentation.

Table I lists in ascending order the value for what roughly appeared to be the average diameter of all of the particles in a heavily populated area of Figure 2, *A*. In some cases, the particles seem roughly spherical, and apparent

diameters can be measured. However, estimation of a size distribution awaits further investigation of shapes, perhaps by inspection of the shadows cast when a beam of a metal or silica vapor is directed obliquely on to the polymer films[38]. Naturally, the true size-distribution can best be shown by volumes rather than lengths.

Apparently these particles, distributed in high conversion or undermodified GR-S, do not weld into the continuous sol phases. They accordingly influence cut growth[39], and, because of their intrinsic high modulus, the modulus of a final vulcanizate.

The microgel in Figure 2 and the underlying thin film of sol may account for the nodular structure exhibited in electron micrographs of other specimens of rubbers if subject to cross-linkage in the latex state[40]. However, it has also been suggested that such fibrous curds are affected by the method of sample preparation[41].

Other electron micrographs of microgel in Figure 2 confirm the basic concepts.

TABLE I

DIAMETERS OF MICROGEL PARTICLES DEPOSITED AFTER DISPERSION OF ORIGINAL WHOLE POLYMER IN BENZENE

<500 Å.	<1000 Å.	<1500 Å.	<2000 Å.	<2500 Å.	<3000 Å.	<3500 Å.
184	505	1009	1514	2240	....	3120
275	505	1009	1514	2294	....	2130
367	550	1009	1650	2615	....	3212
367	642	1055	1650			
413	734	1101	1743			
459	779	1193	1835			
459	826	1285	1927			
	918	1331				
	964	1376				
	964	1376				
		1376				

In *B* appear the largely discrete macromolecules in an undermodified polybutadiene. The microscope specimen was again prepared by deposition from a dilute solution in cyclohexane onto a silica film. Here, numerous particles less than 400 Å. in extent are evident. When the same microgel polybutadiene was deposited from more concentrated solution, structures like those in *C* were characteristic. In fashion possibly precursory to continuous film formation, the microgel molecules (mixed with 14 weight-per cent of more or less chainlike molecules also present) associated into a loose net. Many individual molecules making up this net are visible. This is again interesting evidence of the agglomeration of microgels. *D* depicts the fine-grained microgels made from the emulsion copolymer of methyl methacrylate (93.2 weight-per cent) and ethylene diacrylate (6.8 weight-per cent). This copolymer was taken to 84.4 per cent conversion in 5 hours, at 50° C, using 0.435 weight-per cent of potassium persulfate as catalyst. A 0.5 per cent soap (Rubber Reserve) solution was the locus of polymerization. The electron micrograph specimen was deposited from acetone solution, and individual molecules are difficult to resolve, although the familiar net formation is striking.

SEDIMENTATION OF MICROGEL

In the synthetic rubber program, microgel has been determined by sedimentation after a particular type of agglomeration. The scheme used was

really inverse, inasmuch as whole solid polymer was in contact with a solvent (usually of lower density, such as benzene) for the ungelled portion. With suitable precautions, the microgel aggregate is left as a separate, sedimented layer from which the sol has diffused into true solution[42]. Care to avoid dispersion of microgel during dissolution of sol is crucial. It involves destruction of colloidally peptizing interfaces, such as from soap and fatty acid, water, etc., which may have been retained after coagulation of the original latex[34]. Precise separation may also require chemical formation of a tenuous macrogel network which holds the microgel together. These effects are being thoroughly studied[43].

Careful control of oxidizing conditions is essential preceding this sedimentation of microgel if done by introduction of a loose, continuous network of new primary valence cross-links, which selectively convert the microgel particles into macrogel[44]. Statistically, this selection of larger particles is probable[16], but it is necessary to ensure that, say, mild oxygen-induced gelation by heating in air does not also cross-link or alter (as by degradation) previously ungelled species.

TABLE II

SOL-GEL PROPERTIES OF GR-S CONTAINING MICROGEL, IN SOLVENTS MISCIBLE WITH ITS CHAINS (25° C)

Solvent	Gel content of GR-S (%)	Swelling volume	φ, Vol. fraction of polymer in swollen gel	In η_r/c of sol.
Chloroform	49	47	0.020	0.87
Ethylbenzene	50	45	0.021	0.71
Chlorobenzene	55	40	0.021	0.82
Carbon tetrachloride	52	42	0.022	0.83
Toluene	55	38	0.022	0.79
p-Cymene	52	38	0.023	0.65
Cyclohexane	53	34	0.026	0.71
Benzene	55	34	0.025	0.76
n-Heptane	50	17	0.051	0.41
Dibutyl phthalate	51	16	0.053	...
Amyl acetate	52	16	0.054	0.40

Despite these variables, Table II and Figure 3 show that microgel may be determined in a variety of organic liquids by its sedimentation properties. The sol-gel values on a single carefully prepared and controlled GR-S polymer were obtained in the regular cell[45]. In the case of heavy solvents like chloroform, the microgel aggregate was collected on the bottoms rather than tops of the screens. The results in Table II are typical of many samples studied. The liquids chosen meet the criterion for a suitable solvent, that it be infinitely miscible at room temperature (at least over the chain length range encountered in practice) with ungelled, or sol, species—that is, in the expression:

$$\Delta F_{\text{soln.}} = \Delta H_{\text{soln.}} - T\Delta S_{\text{soln.}}$$

spontaneous dissolution, occurring when ΔF is negative, is favored either by $-\Delta H$ changes, or small ΔH changes which permit the $-T\Delta S$ term to dominate. The free energy of dilution must also be negative. Solvents chosen appeared to fit these conditions.

The entropy term is effective in an osmotic pressure which prevents accumulation of the sol molecules at the bottom of a solution (of lower density) by sedimentation[46]. However, if a liquid such as ethanol were used as solvent

for GR-S, the energy term, ΔH, would be so unfavorable that the polymer chains could not separate from each other, and obviously solubility would no longer be a criterion of lack of cross-linkage or sedimenting networks.

On the other hand, mutual restraints from the cross-links in the microgel network presumably reduce vastly the entropy gain on solution available to a microgel unit compared to a linear chain[47]. This factor may be large in determining exactly at what particle weight microgel separates from solution under gravity alone. Thus the decrease in entropy of dilution, ΔS_0 caused by cross linkage[48] is suggested by:

$$\Delta S_0 = -\frac{R\rho_r V_0^{1/3}}{M_c} v_r$$

Here, R = gas constant, ρ_r = polymer density, V_0 = molar volume of solvent, v_r = volume fraction of polymer, and M_c = molecular weight of chain sections between cross-links.

Accordingly, microgel containing many cross-bonds, wherein M_c is small, has a much decreased entropy of dilution even in a good solvent. The equilibrium swelling volume as $\varphi = v_r$, in Table II, of microgel aggregates has also often been used to estimate M_c, or the tightness of density of the network in microgel molecules.

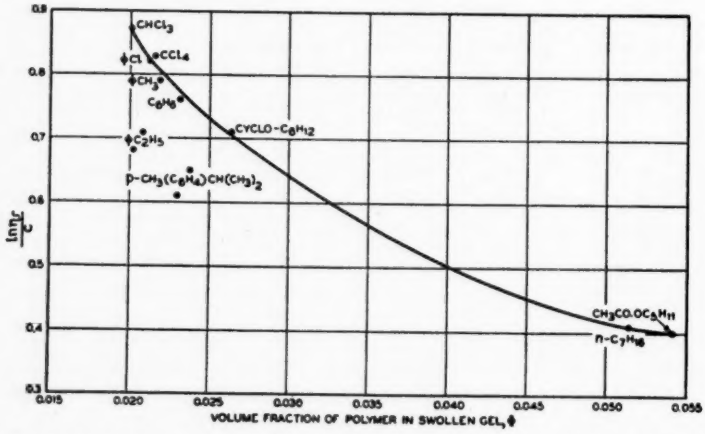

FIG. 3.—Relation between dilute solution viscosity of sol fraction and swelling volume of agglomerated microgel fraction in each of a series of solvents. Virtually same fraction of agglomerated microgel separated by each solvent.

The reasonable constancy in weight-per cent of gel collected identifies it as a distinct and characteristic element of structure. But the variations in φ, and ln η_r/c (for $c \sim 0.1$ gram per 100 cc. of solution), for the sol fraction demonstrate that the solvents of course do not all act the same on the system. These differences, however, affirm the concept of microgel as a cross-linked unit. Figure 3 exhibits a smooth relation between the dilute solution viscosity of the ungelled portion of the polymer molecules and the extent to which the same solvent swells the microgel aggregate. Just such a correlation[49] is expected from the ideas that high ln η_r/c values are obtained from solutions which contain relatively loosely kinked chains[50]. These same solvents would swell gels most, whereas solvents causing tightly coiled chains (such as mixed polar-

nonpolar solvents leading to precipitation) would yield low $\ln \eta_r/c$ and high φ values. Indeed, separate extremes of nonpolar and polar structure seem to fix the positions of *n*-heptane and *n*-amyl acetate in Figure 3.

The swelling of gels has been even more explicitly considered in terms of the energy of the interaction with the swelling liquid[51]. Its effect appears in extensive measurements of the amount of swelling of vulcanizates by a variety of organic liquids[52]. Empirically, one may write[24]:

$$\frac{T\Delta S}{\varphi^2} \sim k_0$$

where ΔS is the entropy gain the gel can achieve by mixing with the solvent despite its cross-linkage constraints and elastic back reaction. The factor affecting φ in Table II must be k_0, and this represents simply the relative mole cohesions of the solvent and the polymer[24]:

$$k_0 = \alpha V_s \left[\left(\frac{E_s}{V_s} \right)^{1/2} - \left(\frac{E_p}{V_p} \right)^{1/2} \right]^2$$

where V_s = molar volume of solvent, E_s = mole cohesive energy of solvent, V_p = molar volume of polymer, E_p = mole cohesive energy of polymer, and α = function of volume fraction of polymer present.

Because the liquids noted in Figure 3 have notably different E_s values (as judged, say, from heat of vaporization), their swelling of microgel would vary on this basis. Thus, the varying φ and $\ln \eta_r/c$ values in Table II reflect nothing more than the interaction energies roughly formulated above. They do not indicate any arbitrariness in the sol-gel characterization of synthetic rubbers beyond the fact that the values from benzene are now customarily used for correlation with physical properties, processing, etc.

Incidentally, the points which fall off the curve in Figure 3 are for liquids whose viscosity properties ($\Delta E_{\text{flow}}/\Delta E_{\text{vap.}}$, for example, where ΔE represents the activation energy for flow, and heat of vaporization, respectively) are unusual.

The sol-gel separation discussed above ultimately depends, after heats of solution are accounted for, on the size of the microgel or its aggregates. First, on the basis of sedimentation equilibrium, the number of kinetic particles, n, expected to occur at height h in a fluid, is related to the number, n_0, at the bottom (of a container with less dense fluid), by:

$$\ln \frac{n}{n_0} = -\frac{N}{RT} \times \frac{4}{3} \pi r^3 (\rho_P - \rho_F) g h$$

where N = Avogadro's number, r = radius of particle, assumed to be a sphere, g = gravity acceleration, ρ_P = density of particle, and ρ_F = density of fluid.

Aggregates of microgel particles which may form aid the size factor. On the other hand, swelling diminishes the $\rho_P - \rho_F$ factor to small importance, over the range afforded by common solvents, at least. Thus, it is just a matter of when the RT factor (corresponding to the osmotic pressure mentioned before) can overcome the r^3 factor. For example, in a cell 10 cm. high, GR-S microgel swollen 64-fold in benzene, so that a particle has a radius of 2000 Å., should still have a concentration at the bottom of the cell $\sim 10^7$ higher than at the top. (Convection currents generally disrupt this gradient, and such microgel particles can usually be considered to form a true solution.)

On the other hand, the sedimentation velocity is so slow as to favor the impression, if one started with a good dispersion of even large microgel (as from vistex solvent), that it would not sediment at all. The sedimentation velocity is:

$$V = \frac{2r^2(\rho_P - \rho_F)g}{9\eta}$$

where the quantities are as shown except that η, the viscosity of the medium, has been introduced[53]. The effective viscosity, η, is apparently fairly large for a swollen sphere of microgel. It might be approximated by the Einstein expression $\eta sp = 2.5\varphi'$ where φ' would now be the volume fraction of the liquid occupied by the swollen microgel. As this can be more than 100 times the volume fraction of the polymer segments alone, 0.002 volume fraction of such microgel, in which $\varphi = 0.2$, would have η_r, in benzene at 25° C, of 1.5. An observed value, for this actual concentration of microgel with somewhat smaller φ' is 1.62, so even other factors enter to increase the denominator of the above expression. Hence, sedimentation velocity is low even in fairly dilute solutions. This considerable viscosity is also illustrated by viscosity measurements on concentrated solutions. Such slow sedimentation may possibly be observable in dispersions of large microgel particles, on standing, by decrease in total turbidity (change in scattering at one angle may be misleading). Thus, a dilute dispersion of microgel had relative turbidity, τ_r, as follows:

After agitation	$\tau_r = 0.306$
After 20 hours' standing	$\tau_r = 0.288$
After reagitation	$\tau_r = 0.304$

It appears, therefore, that experimentally observed retention of microgel at the bottom of a vessel containing a less dense solvent means that the entropy gain on mixing cannot overcome the weight of the particles. However, if the particles are dispersed mechanically, their sedimentation is exceedingly slow.

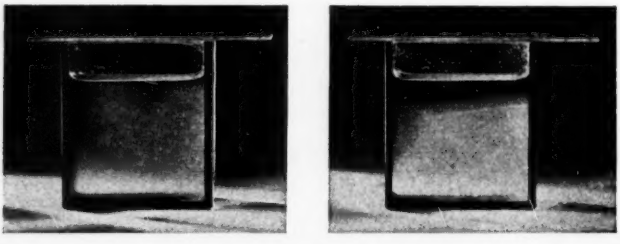

FIG. 4.—Dispersion of 0.24 volume % of coarse microgel in benzene. *Left.* After stirring. *Right.* After settling to apparent equilibrium under gravity. High turbidity is characteristic.

Figure 4 illustrates settling, by standing for 16 hours at room temperature, of slightly swollen and rather highly agglomerated microgel. The homogeneous mechanical dispersion, on the left, has a concentration of 0.24 volume-per cent in benzene. The photograph was taken immediately after stirring. The uneven boundary seen on the right, which shows the same cell after settling for 16 hours under gravity, comes from slight convection. The high turbidity of the system is characteristic.

MICROGEL AND MOLECULAR WEIGHT DISTRIBUTION

Macromolecules of the great size and side reaction origin proposed for microgel should have a strong effect on the distribution of molecular weights which would result from the polymerization if microgel were not formed. Thus, as a gelation reaction, formation of microgel is expected to reduce sharply the weight average molecular weight of the fraction of the original chains which remain not cross-linked[30]. This should show up in a fractionation of the polymer. Ordinary fractionations by precipitation from solution are usually unsatisfactory with copolymers. Indeed, work with J. H. Heiss has shown that varying styrene content in GR-S causes solubility changes comparable to those caused by varying chain length. Hence, fractionation just according to molecular size is not obtained. Even more serious is the problem of isolating fractions so reactive as polydienes are. Thus, a different criterion of molecular weight distribution, the fractional adsorption of polymers from dilute solutions, was used.

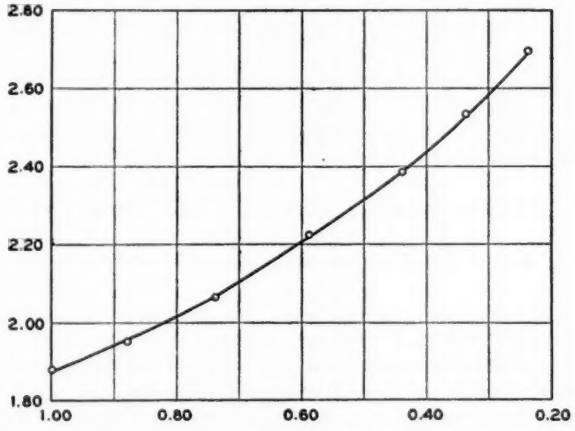

FIG. 5.—Effect of carbon black on solution of polymer containing 19% microgel. Microgel acts like macromolecule during fractional sorption of GR-S from benzene solution (also containing 81% sol), by fine (Halo-C) carbon black. Inherent viscosity of fraction remaining in solution reflects influence of microgel on molecular distribution.

Figure 5 illustrates the interaction[54] when such an adsorbent, fine carbon black, is added with convenient stirring to a dilute solution of Halo C GR-S containing 19 per cent microgel. A similar fractional adsorption curve is shown in Figure 6 for GR-S modified so that it contained no microgel. These curves represent the function $\ln \eta_r/c$ of the solution against weight fraction of polymer remaining dissolved. Now, the fraction of polymer sorbed and sedimented is virtually linear with the proportion of carbon black added to the original solution, as shown in Figure 7 and expected from Gibbs' adsorption isotherm. Hence, the abscissas of Figures 5 and 6 also denote the proportion of carbon black added to the solution. Most of this carbon black settles out, and sorbs on it a considerable portion of polymer[55]. It is significant that no break appears in Figure 5 as compared to Figure 6. The numerical difference in the curves reflects the expected effect of microgel on molecular-weight distribution. Apparently, it is similar to the influence of network formation on a macro

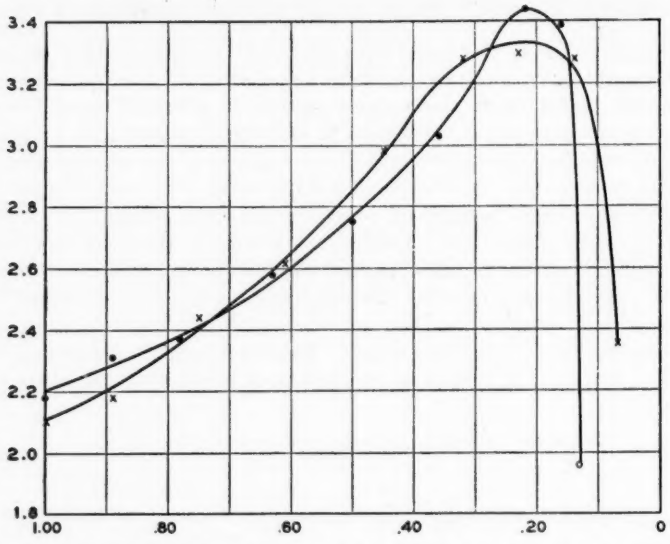

FIG. 6.—Effect of carbon black on solutions of polymers free from microgel. For comparison with Figure 5. Fractional sorption, on carbon black, of GR-S containing no microgel exhibits similar curves displaced by altered molecular weight distribution.

scale[16]. Any particular $\ln \eta_r/c$ in Figures 5 and 6 comes from the summation of fractions, $\ln \eta_r/c = \sum_1^n [\eta]_i f_i$, where f_i is the weight fraction of the ith species, and $[\eta]$ is its intrinsic viscosity. Accordingly, if a particular relation of $[\eta]$ to molecular weight is assumed, a rough characterization of molecular heterogeneity is obtained. (Incidentally, some of the very finest carbon particles form suspended sorption complexes with the polymer. These complexes thus contain swollen, bound polymer of large effective volume fraction. Then, sedimentation becomes extremely slow, and the dispersions remain as dusky or black liquids without settling under gravity, for at least 2 or 3 years. In the

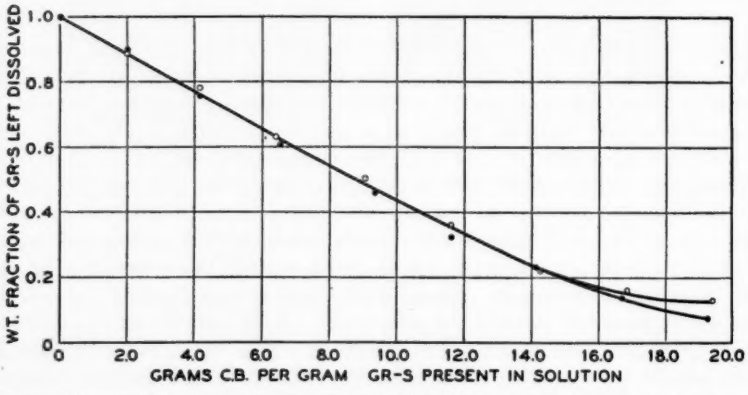

FIG. 7.—Characteristic relation between amount of GR-S remaining dissolved and proportion of carbon black added to solution. Monarch-71 carbon black added to xylene (75)-pyridine (25), a vistex solvent.

absence of polymer, these carbon blacks do not form such stable suspensions in the liquids used.)

In Figures 5 and 6, ln η_r/c of the solutions increases continuously as carbon black is added (complex is formed). Evidently the smaller molecules are first adsorbed. In this case, whatever its own contribution to the inherent viscosity is, the microgel does not perturb the form of the fractional adsorption curve, as compared to the microgel-free case in Figure 6.

The type of molecular-weight distribution shown with increasing proportions of microgel (70 to 80 per cent) accompanied by the remaining low molecular weight material has led to the striking technical properties of GR-S-60[56]. Here, microgel content is conveniently controlled by addition of divinylbenzene rather than by the secondary butadiene cross-linking alone. Microgel units do not orient much on extrusion, tubing, or calendering under high shearing stresses, unlike chain molecules. Accordingly, when suspended in a carrier of fluid, relatively short chain material (which also does not orient notably under shear), unique processability[57], sometimes claimed to be smoother than that of natural rubber, results. Shrinkage is minimized; on the other hand, dynamic properties (dynamic tenacity, such as cut growth) are generally worse. In any case, the microgel molecules in suitable molecular-weight distributions confer wholly characteristic physical properties, in further confirmation of the new macromolecular structure they represent. The now well known smooth flow and thermoplasticity of GR-S-60, which contains a major fraction of microgel networks, is indeed novel behavior compared to the infusibility and intractability so familiar with macrogel or infinite networks.

The eventual drop of ln η_r/c in Figure 6 occurs perhaps when everything except the most highly branched molecules have been adsorbed and removed. The inherent viscosity of these highly branched species is relatively low.

For completeness in discussion of Figures 5 and 6, and their implications, it should be noted that adsorption from synthetic rubber solutions on some carbon black sometimes follows an opposite course. In Figure 8 ln η_r/c were measured for gel-free GR-S dissolved in benzene to which were added (with usual agitation) increasing proportions of a different, somewhat coarser carbon black, Monarch-71. Here, apparently preferential removal of large

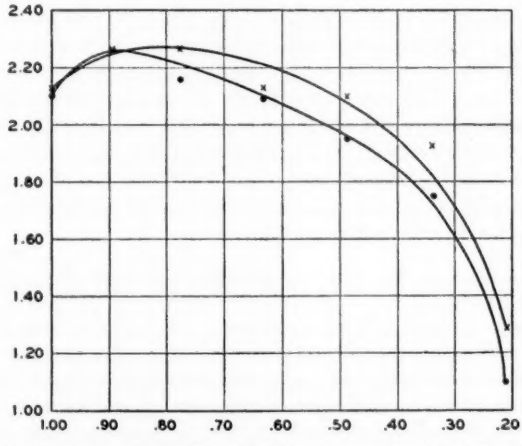

FIG. 8.—Reversed selective sorption of GR-S by Monarch-71 carbon black from benzene solution. Large molecules appear to be taken out first.

molecules by the sorbent occurs. The slight maximum in Figure 8 may mean that branched molecules of lower $[\eta]$ are removed by the first portion of carbon black, again the opposite conduct to that in Figure 6. (If any appreciable fraction of branched but not netted molecules is present, then it probably comes from a different reaction than the one depicted earlier for microgel formation.) This opposite behavior is influenced by the solvent from which the adsorption occurs. Polar solvents like xylene-pyridine mixtures often favor the process of Figure 8.

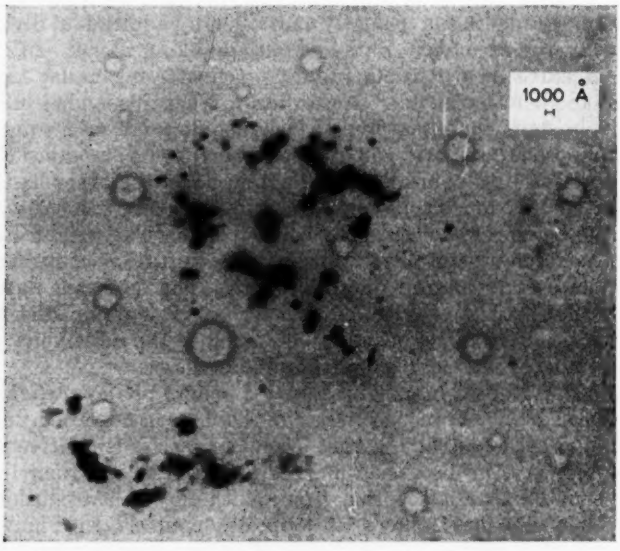

FIG. 9.—Electron micrograph of wetting of fine carbon black by GR-S polymer (21,600×). Sorption complexes which remained suspended in benzene were then deposited on silica supports for micrograph.

Figure 9 shows an electron micrograph of a carbon black-GR-S complex which was deposited on a silica film evaporation of a dilute dispersion in benzene. Thickened regions where the polymer is associated with the denser carbon black are clearly evident. Sorption forces do not extend throughout these polymer layers, but local affinity at the surface of the filler (wetting) is suggested. Similar diagrams in which microgel like that in Figure 2 was also present indicate that even fine carbon black will not penetrate microgel. Thus, the volumes of chain segments comprising the microgel fraction of a synthetic rubber receive reduced reinforcement from fillers, particularly carbon black. Tenacity will accordingly decline.

DIFFUSION AND COHESION OF MICROGELS

In this survey of microgel as an element of polymer structure, its appearance, size, and sedimentation or solution behavior have so far been remarked. Finally, the adhesion of microgel particles to each other and the significance of rate of separation of such particles by diffusion should be noted.

In addition to its sedimentation by gravity, microgel, once agglomerated[58], may also appear to dissolve very slowly because of a slow diffusion rate. This

rate, as follows, depends on D:

$$\frac{dc}{dt} = -Dq\frac{d^2c}{dx^2}$$

where dc/dt = quantity diffusing per time dt, q = cross-section of diffusion cylinder, x = distance, and D = diffusion coefficient.

Recent suggestions for the evaluation[53] of D indicate that it is small for microgels, and depends on their molecular weight to between the 1 and 1/3 power. The actual magnitude of D for these structures may be estimated[53] in the form:

$$D = \frac{kT}{6\pi\eta R_s\psi(\sigma)}$$

The symbols here have the usual meaning; η = viscosity of solvent and R_s = radius of the molecular sphere $\approx \left(\frac{3Q}{4\pi}\right)^{1/3}\left(\frac{18}{5}b^2n\right)^{1/2}$. Here Q = number of cubical cells making up microgel network, b^2 = factor relating R_s^2 to the number of atomic groups, N, making up the macromolecule, while n is the number of such groups between cross-links (represented by the corners of the cubes). Finally, $\psi(\sigma)$ is the factor multiplying R_s which converts the term $R_s\psi(\sigma)$ to the radius of a solid sphere with actual frictional coefficient of the microgel molecule. σ itself is $R_{s/L}$, L being the Debye shielding length. This shielding length accounts for the velocity gradient in the solvent caused by straining through the polymer molecule. Thus, L = distance in from surface of molecular sphere along a radius R_s at which velocity of flow of solvent has fallen to $1/e$ the value it would have far away from the polymer molecule. Evaluation of the whole factor, $\psi(\sigma)$, brings in the molecular weight as noted above, and D for swollen microgel molecules is accordingly low.

The difficulty of stepwise or segmental diffusion of microgels compared to chains would also make study of the temperature coefficient of diffusion interesting.

Large particles with pendant chains, such as are assumed for microgel, may adhere to each other. Their separation demands breaking of many chain end entanglements and segments at once. Even when highly swollen, the summed adhesion of all these attractive centers in two microgel particles could cause a considerable force between them. This effect of molecular size and structure on the heat of solution seems to appear particularly in the properties of polar polymethyl methacrylate microgels, and reduces their solubility.

Both of these factors above were suggested by the data on thixotropy[59] in Figure 10. The ordinate of Figure 10 is converted to absolute units of viscosity by:

$$\eta = 4.331 \times (\text{seconds})$$

The increase in viscosity of the system (measured at low shearing stresses) on standing after stirring (thixotropy) indicates time-dependent interaction of the polymer units—that is, particular association of even the chains of gel-free polymer seems to reflect the adhesive forces noted above, while the slow attainment of this association suggests the low diffusion rate. Accordingly, the sample of curves C on Figure 10 containing 23 per cent of highly swollen microgel ($SV \sim 150$ on the agglomerate) shows the slowest readjustment (compared to the gel-free samples) after its association was destroyed by the shear

of the special, sealed, magnetic stirrer used. Furthermore, the abscissa of Figure 10 shows how this thixotropy is reduced by addition of small amounts of a polar molecule, such as acetic acid. This nonsolvent material presumably increases compaction of the polymer units by causing tighter coiling in the chains and networks. (The action is that caused by poor solvents in Figure 3 to reduce the inherent viscosity.) Hence it reduces chance of entanglement and intimate association of chain segments.

The particularly slow readjustment of the microgel units is strikingly exhibited by the failure of even added acetic acid to cause equilibrium in 15 to 20 minutes, although this was accomplished in the gel-free cases. Residual adhesion of the macromolecules to each other may sustain this thixotropic structure.

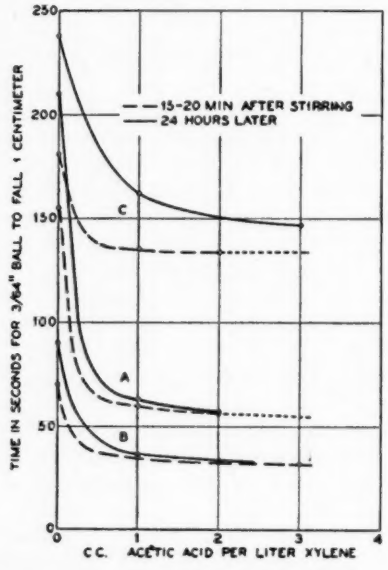

FIG. 10.—Persistence of thixotropy in 17 weight % solutions of GR-S in xylene caused by microgel (curves C). Small additions of nonsolvent acetic acid nearly eliminated thixotropy in gel-free polymers but not in presence of microgel. Viscosities of solutions are at 25° C, and at very low shearing stresses.

The pronounced thixotropy of solutions of GR-S containing 14 per cent of microgel also appears in Figure 11. Here, the viscosity of equally concentrated (~15 per cent) dispersions is plotted against the time in hours after the system was stirred. The work necessary to stir the systems falls in the same order as the curves in Figure 11. The results support the idea that a polar environment greatly aids dispersion, whether by colloidal peptization or reduction of entangling of the gel particles. Likewise, as in Figure 10, such environment hastens equilibration after dispersion. Practically, the power of small proportions of polar molecules in dispersing the polymer emphasizes the care that must be taken in gel separation or microgel agglomeration. The effect of water and alcohols has been long known for natural rubber[60], and may reflect both colloidal and $\Delta H_{soln.}$ variations[29]—for example, polydienes once exposed to air and probably those prepared with catalysts yielding OH radicals, contain hydroxyl groups. These may form hydrogen bonds, which pure benzene

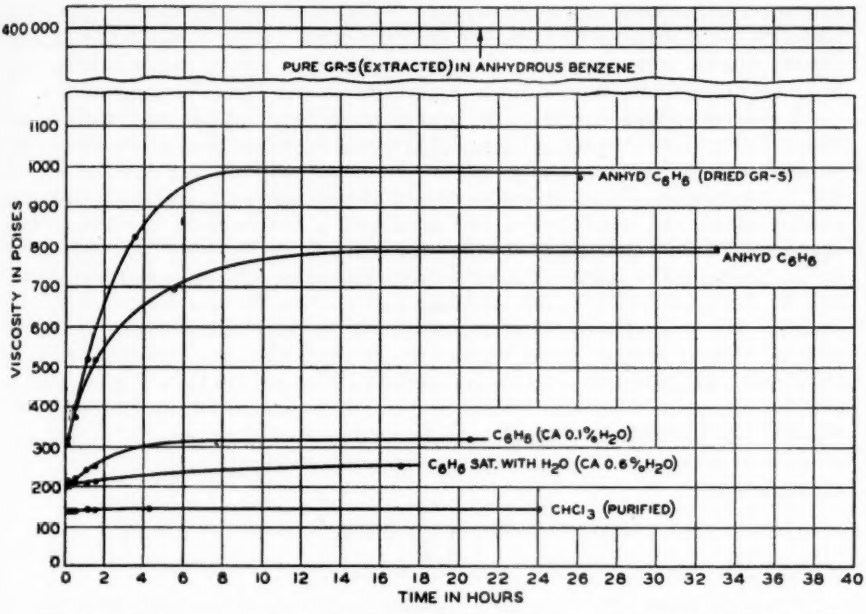

FIG. 11.—Further evidence of disaggregation of microgel by nonsolvents, such as water and fatty acids. Shown by viscosities of 15 weight-per cent dispersions of GR-S containing 14% microgel in benzene and chloroform. Viscosities at 25.0° C plotted against time in hours after initial stirring.

cannot disrupt, but which a little water or alcohol dissolves. Because microgel contains many chain ends, polar agents breaking these dipole attractions also aid dispersion. Other results of slight oxidation also increase the solubility of the polymer in more polar solvents; thus it has been estimated that when all the double bonds in Hevea rubber are replaced by epoxide oxygen, the mole cohesion is increased by about 30 per cent[61].

CHARACTERIZATION OF DISSOLVED MICROGEL

The preceding observations may rationalize the separation of agglomerated microgel, and its characterization by swelling volume by the familiar diffusion-sedimentation methods. However, this is essentially an empirical scheme which, with the proper separation cell, has been shown by nation-wide cross-checks to give consistent and significant results. Nevertheless, a particularly attractive aspect of microgels is that now for the first time the solution properties of cross-linked structures can be studied.

Measurement of the viscosity behavior (especially by the vistex technique) of dispersed microgel reveals interesting behavior, such as positive slopes of $\ln \eta_r/c$ *vs.* c curves (Figure 12). Future studies may show methods of estimating swelling volume from such data, combined with knowledge of absolute molecular weight.

Light-scattering technique was primarily desired to determine microgel, and the classic development of Debye[62] has provided a powerful approach. The size of the swollen particles is enough to cause large dissymmetry around 90° of intensity of light scattered by microgel dispersions[63]. Thus, use of the vistex method in obtaining microgel dispersions (so that the severe practical compli-

cations of antioxidant are avoided) may be followed by measuring of the large particles (as distinguished from the sol molecules) by light scattering at particular angles. In any case, the light-scattering results again affirm the presence of a supermolecular unit, in agreement with the microgel concept.

A polybutadiene was prepared and characterized in this way with J. H. Heiss of these laboratories. Using 0.2 per cent dodecanethiol as modifier with potassium persulfate as catalyst for the emulsion polymerization, after 80 per cent conversion at 50° C, the polymer had 86 per cent microgel which could be agglomerated and separated in the usual cell. The swelling volume of this aggregate, in benzene, was 15. Light scattering from dilute solutions prepared by partitioning the microgel directly from the latex into pure clarified cyclohexane was measured with photoelectric and photomultiplier devices of special design. Dissymmetry of scattering about 90° to the incident beam, intensity of scattering at various wave lengths, at 90°, and absolute turbidity, τ, were obtained. All indicated, when interpreted by the current theory, that microgel, with average molecular weight in the range expected from previous discussion, was present. With as accurate corrections (of exponent of λ, etc.) as possible at present, M, weight average molecular weight, was evaluated from the equation[63]:

$$H\frac{c}{\tau} = \frac{1}{M} + 2Bc$$

First, the term $\left(H\frac{c}{\tau}\right)_{c\to 0}$ (H = optical constant, c = concentration, τ = turbidity) was obtained at infinite dilution, as the plot of $H\frac{c}{\tau}$ *vs.* c was found to be linear at least down to 0.005 per cent. Then, an M_w of 19×10^6 was found, presumably indicating some of the largest soluble molecules yet synthesized.

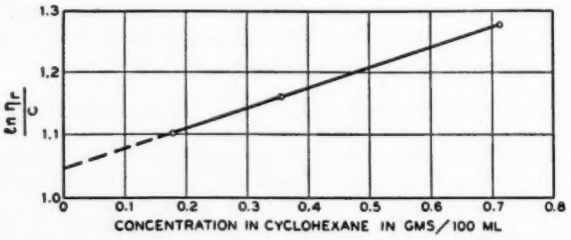

FIG. 12.—Dilute solution viscosity of polybutadiene microgel.

Microgel solutions show unique inherent viscosity properties. The microgel molecules provide models intermediate between loose, coiled, chains yielding Staudinger-Kuhn viscosities, and the hard spheres of Einstein viscosities. For instance, the polybutadiene discussed above has $[\eta] = 1.05$, in cyclohexane (see Figure 12), whereas the value would probably be between 10 and 20 if chains with similar molecular weights were present. Indeed, the fascinating effects of polymer structure on $\ln \eta_r/c$ are conveniently shown in Figure 13. Here, $\ln \eta_r/c$ of vistex solutions of GR-S appears over a wide range of monomer conversions. The curve to the left of the maximum rises steeply as average molecular weight increases (modifier is used up), in roughly chainlike structures. Then, microgel begins to form, and although it is all present in solution,

the total ln η_r/c values fall off because the inherent viscosity of the microgel itself is low. As more and more microgel forms (and its cross-linkage density probably increases), the ln η_r/c values go lower and lower. Thus, we have the interesting case of intrinsic viscosity decreasing as molecular weight increases because of a change in molecular structure (the potassium persulfate catalyst, as well as growing chains, intensifies microgel formation).

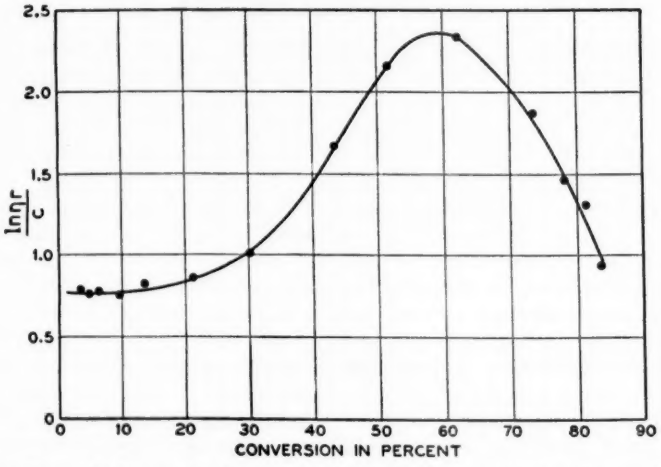

FIG. 13.—Curve of inherent viscosity, ln η_r/c, as function of per cent polymer conversion in GR-S system, obtained by vistex technique. Maximum marks microgel formation, whose structure then causes progressively lower inherent viscosities, although average molecular weight in system continues to rise rapidly.

Curves with the shape of those of Figure 13 are also obtained when microgel is separated out of the solution. This is for the reason discussed in connection with Figure 5, that microgel, as with other gelations[64] incorporates the longest chains, leaving much reduced weight average molecular weight in the sol residue. Then, obviously, the inherent viscosity of the separated sol (microgel-free) rapidly declines. A distribution effect, rather than the structure effect of Figure 13, predominates.

MICROGELS IN GERMAN TECHNOLOGY

The technical as well as scientific significance of microgel in synthetic rubber, coupled with virtual founding of this field in Germany, suggest that the German workers were aware of these macromolecules. Certainly they had numerous indications of them. For instance, data of the I. G. Central Rubber Organization at Leverkusen[65] showed plots of osmotic molecular weight against conversion for Buna-S which rose steadily. On the same plots, the viscosity (Fikentscher) K value went through a maximum, which can be explained as on Figure 13, by formation of microgel. This divergence of osmotic and viscosity relations was regarded as anomalous. The report of Garten, from Leverkusen, of October 12, 1944 (considerably after the American sol-gel applications), described interesting model experiments which clearly produced microgels[66]. This report confused microgels with macrogels, and surprise was expressed when emulsion copolymerization of 1,3-butylene glycol diacrylate with styrene produced soluble polymers. Again, the K values declined when very high

molecular weights were (crudely) indicated by the osmotic pressures. This is apparently again the effect of microgel structure. Finally, electron micrographs were taken of the latices of these polymers, having various degrees of modification and proportions of linear molecules. The micrographs showed negligible differences, whereas if the experimenter had taken electron micrographs of the solutions, again the idea of microgel molecules might have occurred.

GENERAL IMPLICATIONS

This phenomenon of limiting molecular weight by the reaction zone (latex particle) may occur in nature. Protein synthesis in heterogeneous systems, and particularly macromolecules in starch grains and glycogen, may be interesting parallels. The author has examined solutions of some starch triesters, which (amylopectin part) seem to be large three-dimensional molecules. Their fractionation suggests further similarity to microgels[67]. Molecular weights of a few millions were indicated for glycogen solutions by the classical (Rayleigh) analysis of light scattering of their solutions[68]. Such solutions may be examined from the microgel point of view to compare viscosities, nonideality of solutions with respect to Raoults' law, etc., with known models. Evidently, a great variety of microgel systems besides those illustrated above can be made. For instance, Neoprene (polychloroprene) microgels are readily prepared, and show interesting solution properties, such as the radically different k' values for inherent viscosity, noted above for other microgels. Vinyl polymer microgels exhibit special processing properties. Likewise the insolubilization or binding of a few chain molecules by fillers such as carbon black creates a small structural unit whose rheological behavior may be understood by comparison to microgel. This microgellike property of nonorientation under shearing stress is apparently important in the increased smoothness of extrusion imparted by carbon black to many rubbers. A new range of properties of polymer solutions, melts, and solids is available.

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J. W. Mullen, II, and R. W. Walker[69] have particularly contributed to these studies.

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PREPARATION AND PROPERTIES OF RUBBERLIKE HIGH POLYMERS. VI. POLYMERIZATION AND DIMERIZATION OF ISOPRENE *

G. SALOMON, B. B. S. T. BOONSTRA, S. VAN DER MEER, AND A. J. ULTÉE

RUBBER FOUNDATION, DELFT, NETHERLANDS

INTRODUCTION

The preparation of polyisoprene has already been discussed[1], while the mechanical properties of polyisoprene have been compared with other polymers[2] and those of the copolymers with isoprene[3] of this series. In the present paper we shall deal with various theoretical aspects of isoprene chemistry. The course of dimerization reactions gives new information on the properties of conjugated double bonds[4]. It is necessary to inhibit polymerization completely before proceeding with a quantitative study of dimerization. We have, therefore, made a survey of a great number of compounds which influence the course of polymerization reactions. The results that differ somewhat from those found with polyvinyl compounds will be discussed in the first paragraph. Incidentally we found that isoprene itself can act as inhibitor in vinyl polymerization, as will be shown in the section on the inhibitor action of isoprene. After discussing dimerization, we shall make some final comments on the properties of polyisoprene and compare our data with the more extensive work of American authors.

EXPERIMENTAL

Two sources of isoprene were used: (1) a product made from natural rubber[5] and purified via the sulfone; b.p. 34.0–34.3° C; $n_D^{20} = 1.4228$; and (2) a trade product purified by distillation; b.p. (760 mm.) 33.8–34.4° C; $n_D^{20} = 1.4217$. The reaction of this isoprene with maleic anhydride gave a yield of 100 ± 2 per cent and the content of active oxygen was 4–6 p.p.m. after distillation. Polymerization and dimerization were carried out in sealed test tubes with 5–10 gram samples. The amount of polymer was determined by precipitation in alcohol. The dimer was finally prepared in 50–100 gram batches, analyzed by fractionation, and identified as the silver nitrate complex and as the hydrochloride (see below).

Dimerization and polymerization rates at high temperatures were followed by measuring the contraction in sealed thin tubes of 20-cm. length. As the viscosity of the dimer is not essentially different from that of the monomer, an increase in relative viscosity in these tubes is a relative measure of polymerization.

Properties of the polymers were compared as discussed in previous papers. Relative plasticity was measured with the steam plastometer. Solubility and

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swelling in chloroform and benzene were used as a measure of cross-linking, while tackiness of the polymer and viscosity of the dilute solution served as a measure of the molecular size. Quality was judged on this basis by a relative scale from 0 to 6: 0 = oily liquid, 1 = viscous plastic, 3 = weakly elastic and soluble, 4 = 3 but partly insoluble, 6 = insoluble, swollen in chloroform and elastic.

INHIBITORS AND INITIATORS

Our first aim was the evaluation of a strong inhibitor suitable for a quantitative study of dimerization. Results are summarized in Table I. The formation of a rubber in the blank takes place even in a tube filled with purified nitrogen, and is probably due to the presence of traces of peroxides. This type of polymerization comes to a standstill after 3 days. One per cent of picric acid[6] inhibits the reaction completely. At higher temperatures, 25°–150° C, picric acid is still very efficient, but a certain amount of resinification takes place in secondary reactions. Trinitrobenzene is nearly as effective; other nitro compounds are inefficient. Metal nitrates, on the other hand, have either as such, or through the formation of nitrites, a considerable initiator activity.

Hydroquinone and pyrogallol (in group B of Table I) are slightly less effective than picric acid. Other quinones do not reduce the yield in comparison with the blank but lower the quality, a result indicating chain transfer

TABLE I

INHIBITOR AND INITIATOR ACTIVITY OF NITRO COMPOUNDS, PHENOLS, IODINE, AND SULFUR COMPOUNDS, AT 100° C WITH PURE ISOPRENE

		Polymer				
		Reaction time				
		3 days		11 days		
No.	Compound	Yield	Quality	Yield	Quality	Type of activity
1	Blank	20	2	21	3	—
	A. Nitro Compounds					
2	Picric acid	0.0	—	0.3	0	Strong inhibitor
3	Trinitrobenzene	3	1	5	1	Strong inhibitor
4	Nitronitrosobenzene	12	1	19	1	Chain transfer
5	Lithium nitrate	33	2	48	4	Initiator
6	Silver nitrate	37	2	66	4	Initiator
	B. Polyphenols					
7	Hydroquinone	0.0	—	3	0	Strong inhibitor
8	Di-*tert*-amylhydroquinone	11	1	15	1	Chain transfer
9	Pyrogallol	2	0	5	0	Strong inhibitor
10	Chloranil	17	1	25	1	Chain transfer
	C. Iodine Compounds					
11	Iodine	8	0	14	0	Chain transfer
12	Iodoform	17	0	16	0	Chain transfer
13	Iodoacetic acid			>16	0	Chain transfer
	D. Sulfur Compounds					
14	Thioacetic acid	14	2	20	2	Chain transfer
15	Thiourea	14	3	26	3	Weak initiator
16	Thiophenol	15	2	34	2	Weak initiator
17	Sulfur	29	2	47	2	Weak initiator

activity. This effect is still more pronounced with iodine compounds (group C of Table I), which yield oils rather than rubbers.

Sulfur compounds (group D of Table I), well known as chain transfer agents,[1] form the borderline between inhibitors and initiators. Sulfur itself has a distinct accelerating action on isoprene.

Our earlier experience[7] is confirmed by the results summarized in Table II. Acids as well as a well known antioxidant (No. 18) act as weak initiators. Peroxides are moderately effective and yield soft and sticky products. Another source of radicals (No. 24 in Table II) is also less active with isoprene than with vinyl compounds.

TABLE II

WEAK AND STRONG INITIATORS FOR ISOPRENE AT 100° C

		Polymer				
		Reaction time				
		3 days		11 days		
No.	Compound	Yield	Quality	Yield	Quality	Type of activity
1	Blank	20	2	21	3	—
	A. Acids and Bases					
18	Phenyl-β-naphthylamine	11	2	30	2	Weak initiator
19	Acetic acid	24	3	49	4	Initiator
20	Acetoacetic ester	29	2	50	3	Initiator
	B. Peroxides and Related Compounds					
21	Benzoyl peroxide	42	2	60	2	Initiator
22	Ascaridole	36	2	62	4	Initiator
23	Tetralin peroxide	49	2	75	2	Strong initiator
24	Tetraphenylsuccinic acid dinitrile	36	2	36	2	Weak initiator
	C. Azo Compounds					
25	Hydrazobenzene	5	1	7	1	Inhibitor
26	Azobenzene	16	2	30	2	Weak initiator
27	2-Methylbenzimidazole	11	1	20	1	Chain transfer
	D. Azoamino Compounds					
28	Diazoaminobenzene	69	4	75	6	Strong initiator
29	Na salt of No. 28	44	3	74	6	Strong initiator
30	*N*-benzyl derivative of No. 28	56	3	75	6	Strong initiator
31	*p*-Diazotoluene-aniline	49	3	73	6	Strong initiator
32	*p*-Diazotoluene-*p*-toluidine	46	3	69	6	Strong initiator
33	Bis-(benzene diazo)-methylamine	61	3	68	5	Strong initiator

The azo compounds (group C of Table II) are likewise of little value, and the only remaining group is the azoamino compounds, which combine the ability to initiate polymerization with the tendency to form cross-links. Diazoaminobenzene is more effective than any of the others in this group. The formation of phenyl radicals is probable an essential step in the initiation.

The well known correlation between reaction rate and square root of initiator concentration has been found to hold also for pure isoprene (see Table III). The high yield after a relatively short time is reached only at the expense of

TABLE III

CORRELATION BETWEEN YIELD AND INITIATOR CONCENTRATION FOR ISOPRENE AT 100° C. USING n PER CENT DIAZOAMINOBENZENE (HALF-TIME FOR POLYMERIZATION IN HOURS)

n, per cent D.A.B.	0.1	0.5	1.0	2.0
Hours	192.	79.	55.	36.
Relative rate	0.31	0.8	1.1	1.6
$\sqrt{n}$	0.32	0.7	1.0	1.4

quality (see Figure 1). Both results are in good agreement with present theories of polymerization.

We have studied the activity of some of the initiators and inhibitors at 150° C with the aim of elucidating the simultaneous occurrence of dimers and polymers at this temperature.

The formation of a very soft polymer induced by 0.1 per cent diazoaminobenzene at 150° C is complete after 2–3 hours. Benzoyl peroxide, on the other hand, is so ineffective that dimerization becomes preponderant. In the presence of 1 per cent of the iodine compounds Nos. 11, 12, 13, or the sulfur compounds, Nos. 14 and 16 of Table I, only 20 per cent polymer is formed; the rest consists of liquid dimers. These reagents, however, interact with the dimers as can be concluded from the presence of sulfur and iodine compounds in the liquid fraction. The only useful inhibitors proved to be picric acid and pyrogallol. The influence of concentration is very pronounced; 0.1 per cent inhibitor at 150° C becomes ineffective, and can even act as a weak initiator of polymerization. With copper oleate such changes from an effective initiator, even at a concentration of 1 per cent to a strong inhibitor at 5 per cent concentration are similar to the effect of concentration in the "antioxygène" studies of Dufraisse and his school.

The difference in the kinetics of high-temperature diene and vinyl polymerization should be emphasized. At 150° C isoprene dimerizes with a half-time of about 4 hours. This reaction is purely thermal and not influenced by the

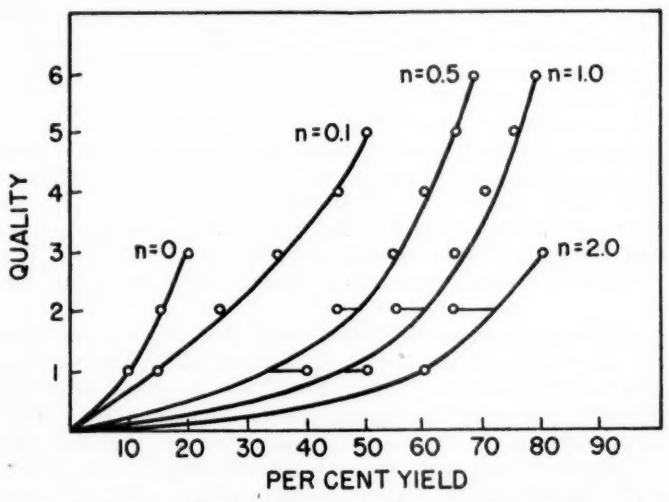


FIG. 1.—Influence of initiator concentration (n per cent diazoaminobenzene) on relative quality of polyisoprene.

presence of an inhibitor. Polymerization can occur only if it is very fast. The molecular size of the polymer is influenced by the inhibitor properties of the dimer[8]. The thermal polymerization of styrene, on the other hand, can be delayed, for example, by the presence of 1 per cent pyrogallol for about one hour. No reaction occurs during this time until the inhibitor has been used. However, a mixture of low viscosity, consisting of solid and liquid polymers, can be produced from styrene by heating it in the presence of 1 gram of iodine or iodoform at 200° C. A polymerization-depolymerization equilibrium seems to be established under the catalytic influence of iodine at 200° C, completely comparable to the action of oxygen at lower temperature[9].

THE DIMERIZATION OF ISOPRENE

We have tried to separate dimerization and polymerization by the action of picric acid. On heating isoprene at 130° C, 90 conversion is reached after 160 hours. The polymers can be separated into 80 per cent dimers and 13 per cent of a rubber (relative quality 3). About 7 per cent higher boiling material and benzene-soluble resins are formed in side reactions. This result

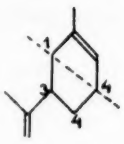
TABLE IV

DIMERIZATION OF ISOPRENE STABILIZED WITH 1 PER CENT PICRIC ACID

Temperature (° C)	Time (hours)	Per cent dimers	Per cent polymers
100	24	11	0
	72	24	0
	168	43	0.2
	408	70	17
	1632	79	21
125	24	42	0.2
	48	59	0.4
	96	70	4.4
	160	84	6
150	0.34	49	0.2
	24	70	5
	48	74	11
200	24	60	32

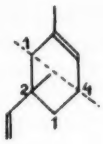
is in good agreement with the experience of previous authors[10]. As expected, it is possible to inhibit polymer formation completely by the addition of 1 per cent of picric acid. Results are summarized in Table IV. No trimers or higher boiling materials are formed at the time of 50 per cent dimerization, but resinification sets in on further heating between 100 and 150° C. The data of Table IV suggest a reaction higher than second order and a large energy of activation.

It has been known for a considerable time that the four possible carbon skeletons of the dimer are formed in different yields. The position of the double bonds in the four isomers is uncertain, due to a possible allylic rearrangement. Lebedev[11] separated the higher boiling mixture, (I) + (II), from a lower boiling compound, to which he assigned structure (III), but which could also be a mixture of (III) and (IV). Wagner-Jauregg[12] proved the preponderance of the diprene I in the higher boiling fractions. We can confirm these results and add the following methods for a quantitative separation.



(I)
Diprene

(II)
Dipentene



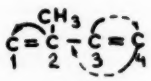
(III)
Lebedev

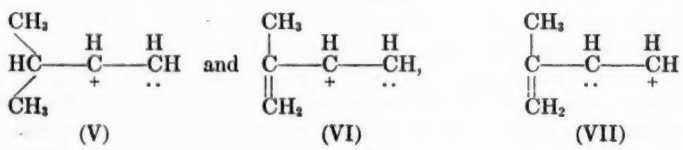
(IV)

a. I can be separated from II by the action of aqueous silver nitrate. I dissolves in this reagent and forms a high-melting complex compound, whereas II neither dissolves nor crystallizes with silver nitrate.
b. The solid (*trans*) dihydrochloride from II has a similar melting point to that of the solid dihydrochloride from I, but on mixing the hydrochlorides a considerable depression is observed. In addition to the solid, an isomeric liquid dihydrochloride from I (probably the *cis* isomer) is formed.
c. III and (or ?) IV are soluble in aqueous silver nitrate but do not crystallize. The reaction with hydrochloric acid yields only a monochloride. The double bond in this monochloride does not add on HCl even at 100° C under pressure; this result is in good agreement with structures III and IV.

A detailed discussion of these results will be given elsewhere, but the following preliminary estimate of yields already permits some new conclusions. Yields: I $\gtrapprox$ 80; II $\lessapprox$ 5; III and (or) IV $\lessapprox$ 10 per cent.

The electronic formulation of isoprene[13] allows for the explanation of the donor properties of the 1-carbon atom and the acceptor properties of the 3,4 double bond[14]. As has already been discussed in another paper[4] the reactivity of the 3,4-double bond at 150° C corresponds to that of the double bond in maleic anhydride at 20° C. The difference in yields indicates that the 3,4-double bond is about ten times more reactive as an acceptor than the 1,2-double bond. While this result is in good agreement with the electronic concept, we find a rather surprisingly large difference in the yields for I and II. The formation of dipentene occurs less readily than the formation of Lebedev's hydrocarbon. In other words the pair of electrons from C-1 add on almost exclusively to C-3 and only very rarely to C-4, thus leading to diprene as the main reaction product. Comparing the structures V and VI:





(V) (VI) (VII)

we can draw the following conclusions.

1. The overall availability of π-electrons in VI is much smaller than in V, this effect being due to resonance.
2. The distribution of charge, making the C-3 atom positive, is the same in both olefins. The direction of addition to the 3,4-double bond in isoprene corresponds, therefore, mainly to the addition rules for polar reactions, involving monoolefins. The reverse structure VII reacts only to a very small but measurable extent isoprene addition and, as far as we know, not at all in other polar reactions such as HCl addition.

POLYISOPRENE

We have already shown[15] that a close correlation exists between brittle point, elastic recovery, and rebound elasticity of polydienes and their copolymers. Two structural factors are of significant influence: (1) methyl groups in the diene, and (2) 1,2-addition or vinyl copolymerization leads to a decrease of molecular flexibility and, therefore, to an increase in brittleness. The importance of the influence of other structural factors on mechanical properties can be deduced from a study of tensile strength. This becomes evident from a recent survey by d'Ianni[16]. Isoprene, polymerized with a special metal catalyts, has a similar content of vinyl side groups (form 1,2-addition) to that of emulsion polyisoprene and a similar brittle point, but a much higher tensile strength. We can confirm these results as far as the properties of emulsion polymers are concerned and can add that the properties of bulk polymers are similar. Polyisoprene made with 0.1–0.5 per cent of diazoaminobenzene had promising mechanical properties as a raw rubber (see Figure 1), but the average tensile strength of a carbon black mixture did not exceed 75 kg. per sq. cm. at 450 per cent elongation at break. In fact we were unable to produce a fair rubber from polyisoprene. This confirms the opinion[16] that polymolecularity as well as unknown details of the chain structure in polyisoprene is essential for a high tensile value.

The addition of hydrochloric acid to the polymer has been used[16] as a measure of the total 1,4- and 3,4-polymerization. We can confirm the usefulness of this method and also that the number of 1,4 + 3,4 polymer units was found to be independent of experimental conditions in bulk and emulsion polymerization.

THE INHIBITOR ACTION OF ISOPRENE

It is a well known phenomenon that a vinyl compound acts as a retarder in the polymerization of a second vinyl compound. This effect is probably due to the intermediate formation of a resonance-stabilized radical, and cannot therefore be explained in general terms. The copolymerization of 1,1-dichloroethylene with dienes and other vinyl compounds has been frequently studied in the course of applied as well as fundamental research. From the available data the impression is gained that this process does not differ essentially from other diene-vinyl-copolymer systems. This is probably true for the propagation step in systems with the diene as the main phase. We have found incidentally that the situation changes abruptly when a small quantity of isoprene is added to dichloroethylene. Figure 2 gives a survey of yields at constant reaction time, and Figure 3 illustrates the inhibitor activity of isoprene during very long reaction times. Even at high isoprene concentrations the propagation chain is essentially carried by the added isoprene. This follows from the composition of the polymers. They show a large deficiency of dichloroethylene units (see Figure 4).

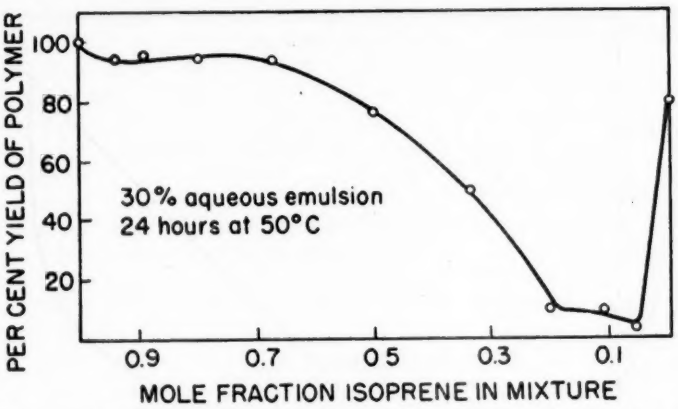
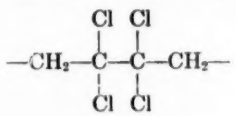


FIG. 2.—Inhibitor action of isoprene on polymerization of pure 1,1-dichloroethylene. One per cent of H_2O_2 with Fixanol as emulsifier.

Kinetic analysis of the products[17] makes it probable that units of the type:



are inserted between the isoprene chains and not only the head-tail structures present in vinylidene chloride polymers. Analogous experiments in bulk polymerization lead to identical conclusions.

Using 1 per cent of diazoaminobenzene or 1 per cent of benzoyl peroxide, it is possible to polymerize dichloroethylene at 100° C in a few hours. Addition of 0.5 mole-per cent of isoprene is sufficient to inhibit polymerization. A few per cent of polymers are formed in the beginning, but the reaction thereafter comes to a complete standstill. One can follow this phenomenon conveniently by measuring the contraction and viscosity of the liquid-monomer mixtures.

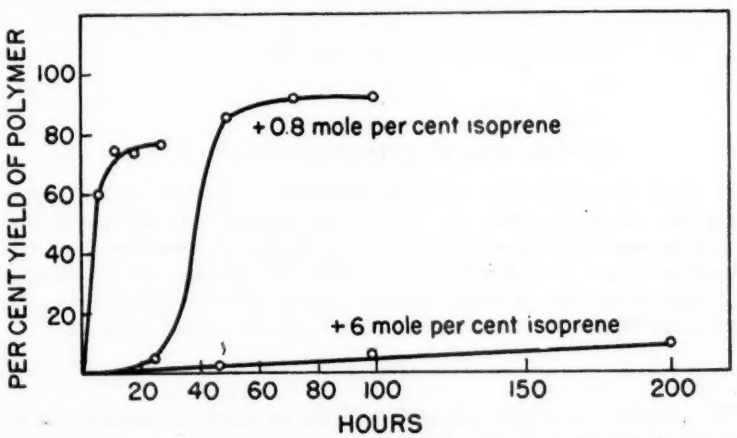


FIG. 3.—Influence of isoprene concentration on inhibitor action in the polymerization of pure 1,1-dichloroethylene (left-hand curve). Emulsion as in Figure 2. Time variable.

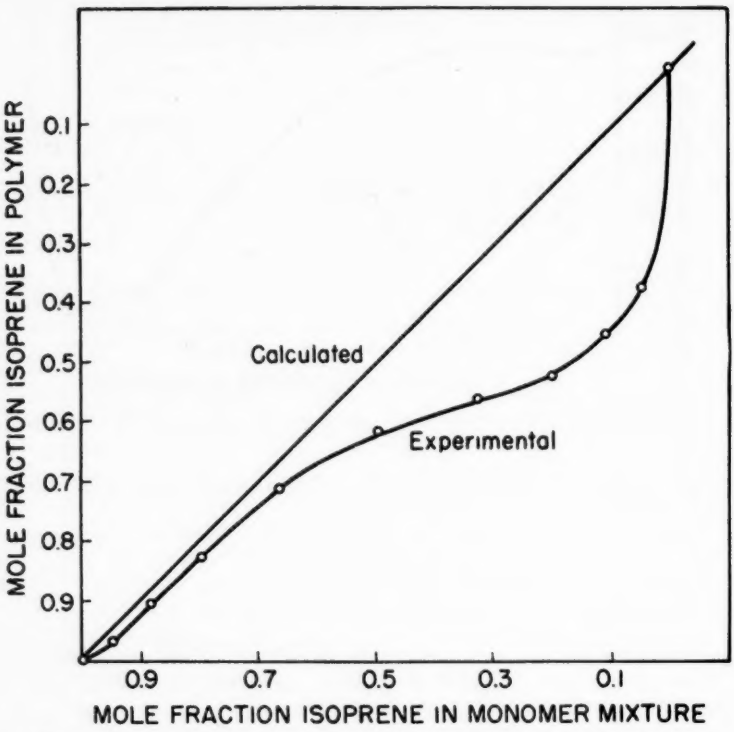


FIG. 4.—Chlorine deficiency in copolymers from isoprene and 1,1-dichloroethylene. Emulsion as in Figure 2. 24 hours at 50° C.

The present knowledge of radical reactivity is, in our view, not sufficiently developed to predict these curious results. A tentative explanation *ad hoc* is the following. The radicals VIII and IX:

(VIII) $$R{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}CCl_2\cdot$$

and

(IX) $$R{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}CCl_2{-}CCl_2{-}CH_2\cdot$$

are so much stabilized that chain termination supersedes chain propagation. Taking the selective action of $-CCl_3$ and similar radicals into account, this explanation seems also feasible in terms of electronic structure.

Another cause of inhibition is an occasional transfer of a hydrogen atom from isoprene to the growing radical chain. The resulting new allyl-type radical from isoprene is too stable[18] to carry on the reaction chain.

SUMMARY

The inhibitor and initiator action of thirty-three compounds on the bulk polymerization of pure isoprene has been studied. Picric acid was found to be the most powerful inhibitor at 100° C. The conclusion reached in Part I that

the initiator activity of diazoaminobenzene is superior to all other compounds has been found to be valid also between 100–150° C. The heat polymerization of isoprene between 100–150° C in the presence of picric acid leads only to the formation of dimers. Three of the four possible isomers have been separated. The solid complex compound of diprene (I) with silver nitrate has been used to separate it from dipentene (II) and the hydrocarbon of Lebedev (III, IV) has been identified as a monochloride. The relative yields (I):(II):(III = IV) of 16:1:2 are in agreement with the relative availability and localization of π-electrons in isoprene. Observations on the properties of polyisoprene are in agreement with the more extensive work by d'Ianni. Some remarks on polymers from bulk polymerization are added. Isoprene acts as a powerful inhibitor on the polymerization of vinylidene chloride. This effect is independent of the method of polymerization.

ACKNOWLEDGMENT

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PREPARATION AND VULCANIZATION OF UNSATURATED ACRYLIC ELASTOMERS *

W. C. MAST AND C. H. FISHER

EASTERN REGIONAL LABORATORY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE, PHILADELPHIA, PENNSYLVANIA

It was shown in earlier papers[1] from this Laboratory that methyl and ethyl acrylate resemble isobutylene[2] in that they can be copolymerized with a small proportion of a polyolefinic monomer, such as butadiene or isoprene, to vulcanizable copolymers. Rubberlike vulcanizates were obtained[1] by compounding the copolymers—assumed to contain olefinic unsaturation—with sulfur and accelerators and molding the compounded stock at approximately 150° C. This finding was followed by an extension of the acrylic elastomer investigation to include (1) the preparation and vulcanization of additional unsaturated acrylic elastomers, (2) the development of special recipes[3] capable of curing ethyl polyacrylate and similar saturated acrylic resins, and (3) a search for functional groups other than olefinic linkages that can be used conveniently for vulcanization purposes[4].

This paper reports the vulcanization of additional unsaturated acrylic elastomers prepared by copolymerizing acrylic esters with a small proportion of eleven dienes, eleven polyolefinic esters, and six ethers (Table 1). The purpose of the work was to prepare improved elastomers, ascertain qualitatively the tendency of the polyolefinic monomers of widely different character to form cross-linked copolymers, and to obtain information on the effect of polymer structure (as determined by the selection of monomers) on the rate of curing and properties of the vulcanizates.

TABLE 1

POLYENES USED IN THE PREPARATION OF ACRYLIC ESTER COPOLYMERS*

Polyene	Boiling point, °C	Percentage equivalent to 2% butadiene†
1,3-Butadiene	-5^{713}	2.00
Isoprene	33.5	2.52
1,3-Pentadiene‡	42–44	2.52
Cyclopentadiene	41–42	2.52
2,3-Dimethyl-1,3-butadiene§	71	3.04
Myrcene‖	68^{23}	2.52
Divinylbenzene	¶	4.84
Alloöcimene**	90^{21}	2.52
2-Methyl-1,3-pentadiene	76	3.04
Chloroprene	59.4	3.27
3-Vinyl cyclohexene	Not distilled	4.00

* Reprinted from the *India Rubber World*, Vol. 119, No. 5, pages 596–598, February 1949; No. 6, pages 727–730, March 1949.

TABLE 1—*Continued*

POLYOLEFINIC ESTERS USED IN THE PREPARATION OF ACRYLIC ESTER COPOLYMERS

Ester		
Allyl maleate	$78^{0.6}$	3.67
Furfuryl acrylate††	93^{16}	2.83
Crotyl acrylate††	60^{23}	4.70
Cinnamyl acrylate††	$108^{1.2}$	7.0
Citronellyl acrylate††	$108^{5.4}$	7.8
Geranyl acrylate††	$116^{6.2}$	3.87
Allyl lactate maleate	Not distilled	6.3
Allyl diglycol carbonate	160^{2}	10.1
Rhodinyl acrylate††	$107^{4.2}$	7.8
4-Methyl-4-penten-2-yl acrylate††	$62^{13.8}$	5.7
Allyl phthalate	150^{1}	

POLYOLEFINIC ETHERS USED IN THE PREPARATION OF ACRYLIC ESTER COPOLYMERS

Ether		
Vinyl ether	39	2.6
Di-allyl glycol	35^{1}	5.26
Allyl ether	94.3	3.62
Methallyl ether	..	4.65
Tetra-allyl-alpha-methyl-glucoside‡‡	$160^{1.5}$	4.36
Allyl starch§§	..	10

* The sources of these monomers are acknowledged at the end of the paper.

† Proportion in per cent of the polyolefinic monomer required to give a copolymer having the calculated vulcanizable unsaturation of a 98 per cent ethyl acrylate–2 per cent butadiene copolymer (assuming one residual double bond).

‡ Prepared in the Northern Regional Research Laboratory by pyrolysis of the corresponding glycol diacetate[5].

§ One of the samples used was prepared by pyrolysis of pinacol diacetate[6].

‖ Myrcene: $(CH_3)_2C{:}HCH_2CH_2C(CH{:}CH_2){:}CH_2$.

¶ Purified by fractional recrystallization.

** Alloöcimene: $(CH_3)_2C{:}CHCH{:}CHC(CH_3){:}CHCH_3$.

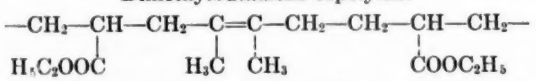
†† Preparation described by Rehberg and Fisher[7].

‡‡ Preparation described by Nichols and Yanovsky[8].

§§ Preparation described by Nichols, Hamilton, Smith and Yanovsky[9].

It would be expected that the unsaturated copolymers[10] obtained with the polyfunctional monomers of Table 1 would differ considerably in structure, leading to differences in curing rate and properties of the vulcanizates. These differences could arise from dissimilarities in both the structure and location of the olefinic linkages. For example, the unsaturation in the 2,3-dimethylbutadiene copolymers should be principally in the polymer chain and characterized by the presence of two methyl groups; whereas the unsaturation in the crotyl acrylate copolymers should be principally in side chains and subject to less steric hindrance (see Figure 1).

Dimethylbutadiene copolymer



Crotyl acrylate copolymer

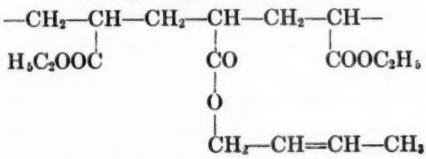


FIG. 1.—Dimethylbutadiene and crotyl acrylate copolymers.

EXPERIMENTAL DETAILS

The polyolefinic monomers (Table 1) were prepared here[2] or obtained from other organizations. When desirable and feasible, the monomers were further purified by washing with alkali and distillation.

The monomers were emulsion polymerized by the method previously described[11]. The polymerizations were carried out in a round-bottom, three-neck Pyrex flask fitted with glass-ground joints for a condenser, water-sealed glass stirrer, and thermometer well. Water and emulsifier were stirred and heated (below 85° C) in the flask until a smooth dispersion or solution was obtained. The monomers were then added, and polymerization was induced by heat and catalysts (Table 2)[12]. Ammonium persulfate was used to initiate polymerization in most instances, but hydrogen peroxide, benzoyl peroxide, and succinic acid peroxide were also used. Acrylonitrile and dodecanethiol were used in some polymerizations to decrease cross-linkage. The emulsions were refluxed during the polymerization, and at refluxing temperature a period of 30 minutes to several hours was usually required. The temperature rose during the polymerization from about 72 to 82° C and from 82 to 92° C when methyl acrylate and ethyl acrylate, respectively, were the principal monomers. Hence the course of the polymerization could be followed roughly by noting the temperature. The extent of polymerization could be followed also by observing changes in the refractive index, density, and solids content of the emulsion. At the end of the polymerization any unchanged methyl acrylate or ethyl acrylate was removed by blowing steam through the emulsion.

The refluxing temperature was lowered at the beginning of the polymerization when low-boiling dienes were used (butadiene copolymers were prepared in pressure vessels). Gentle refluxing was maintained, and the temperature was allowed to rise gradually during the polymerization. In some instances preliminary runs were required to determine the correct amount of catalyst. The minimum amount of catalyst that would cause polymerization within a reasonable time (usually one hour to three hours) was used. It was found desirable to have little or no induction period before the start of the polymerization to reduce the possibility of side reactions of the monomers or emulsifying agents and to prevent excessive precoagulation during the reaction. The monomers were mixed immediately before being added to the aqueous phase or added separately. The addition of sufficient catalyst in one lot to cause polymerization was preferable to several additions of smaller quantities at half-hour or longer intervals because the total required quantity of catalyst was less and side reactions were less troublesome. A period of five to fifteen minutes was usually required to heat the mixture to refluxing, and the induction period could often be reduced or virtually eliminated by adding the catalyst just before heating was started.

When polymerization was considered complete, the latex was coagulated by adding it while hot to twice its volume of hot, rapidly stirred, 5 per cent sodium chloride solution. The resulting fine, discrete, rubberlike crumb was washed five to seven times with hot distilled water. (Washing was continued until the wash water gave a slight or negative test for chloride ion.) No trouble was encountered when the temperature of the wash water was kept above 90° C, but the polymer lumped together and was difficult to wash at lower temperatures. The copolymers were air dried for several days at room temperature. Randomly chosen samples dried in this manner contained less than 0.5 per cent water.

TABLE 2

EMULSION POLYMERIZATION OF DIENE—ETHYL ACRYLATE MIXTURES

Expt. no.	Diene	Percentage						Temperature (°C)	Time (hours)	Yield (%)
		Diene	Acrylonitrile	Dodecanethiol	Ammonium persulfate	Tergitol penetrant no. 4*	Solids			
E31†	Butadiene	2	6	..	0.10	1	25	75–77	5.0	50
E32†	Butadiene	2	6	..	0.15	1	25	75–77	5.0	60
E33†	Butadiene	2	6	..	0.22	1	25	75–77	5.0	70
D45	Isoprene	2.1	..	..	0.13	0.75	25	77–92	0.8	95.5
D46	Isoprene	2.1	6	..	0.09	0.75	25	77–92	1.7	91
D47	Isoprene	2.1	6	0.10	0.09	0.75	25	77–92	1.5	92
D48	Isoprene	4.2	6	0.10	0.10	0.75	25	75–92	1.7	77
D49	Isoprene	8.4	6	0.10	0.14	0.75	25	75–92	2.3	85
D97	Isoprene	2.1	6	..	0.11	0.75	37.5	77–92	3.5	95
D125	Isoprene	2.1	6	..	0.09	0.75	37.5	77–92	7.0	87
D50	Piperylene	2.1	..	..	0.10	0.75	25	78–92	2.2	97
D51	Piperylene	2.1	6	..	0.06	0.75	25	78–92	1.3	91
D52	Piperylene	2.1	6	0.10	0.08	0.75	25	78–92	1.2	94
D53	Piperylene	4.2	6	0.10	0.09	0.75	25	78–92	1.7	91
D81	Piperylene	2.1	6	..	0.06	0.75	25	78–92	2.7	86
D82	Piperylene	2.1	9.3	..	0.075	0.75	25	78–92	5.7	77
D83	Piperylene	2.1	6	..	0.05	0.75	25	78–92	2.5	87.5
E18	2,3 Dimethylbutadiene	2.6	0	..	0.07	1.75	20	77–92	0.7	93
E19	2,3 Dimethylbutadiene	2.6	6	..	0.05	1.75	20	77–92	1.0	90

* Moisture free basis.
† In agitated sealed bottles under pressure.

The solubility characteristics of the copolymers were ascertained, and toluene solutions of the soluble copolymers were prepared and used in the determination of intrinsic viscosity. Insolubility was generally considered evidence of cross-linkage, effected either through the olefinic unsaturation or caused by free radical cross-linkage (initiated by the polymerization catalyst) of the ethyl polyacrylate portion of the copolymer chain[13]. Most of the insoluble copolymers formed loose easily dispersed gels that were entirely different from the gel fraction of GR-S rubber and probably were indicative of a low degree of cross-linkage. The soluble and insoluble fractions of the copolymers were not examined in detail, although a study of the type of gel and the ease of its dispersion might have given significant results.

The copolymers were judged further by their general appearance, the ease with which they could be drawn (manually) into filaments, their behavior on milling, and the physical properties of the vulcanizates. A small rubber mill[14] was used for the compounding (80 to 110° F). The stocks were cured as slabs 0.03-inch thick and tested on a modified Scott L-6 tester. Brittle points were determined by the method of Selker, Winspear, and Kemp[15]. The work reported herein was done before the discovery[16] in 1945 that milling at about 160° F is preferable to milling at lower temperatures.

ETHYL ACRYLATE—DIENE COPOLYMERS

Preparation of the diene copolymers of Table 2 required substantially larger amounts of catalyst than that normally used to polymerize ethyl acrylate[17]. Possibly the retarding effect of the diene and the use of increased amounts of catalyst were partly responsible for the fact that the diene copolymers were different from ethyl polyacrylate in being insoluble in toluene, having a drier appearance and less tack, and in being less easily drawn into filaments. The diene copolymers resembled other ethyl acrylate polymers and copolymers prepared in this Laboratory in that their behavior on being drawn with the fingers into filaments was related to their general appearance and their solubility characteristics. For example, the polymers that could be readily drawn (slowly to allow for cold flow) into threads and eventually into virtually invisible filaments were usually soluble in benzene, toluene, ethyl acetate, dioxane, and similar solvents. The polymers that gave coarse threads having uneven sections usually formed dispersible gels with solvents. Polymers that tore across thick sections and contained lumpy portions in the stretched area yielded less dispersible gels or remained as discrete swollen masses[18].

Butadiene, isoprene, and dimethylbutadiene had diminishing tendencies to form cross-linked copolymers during polymerization, in the order named. Isoprene and piperylene had about the same tendency to form cross-linked copolymers. The best vulcanizates were obtained from the isoprene, piperylene, or dimethylbutadiene copolymers. The vulcanizates from the diene copolymers appeared less lively, that is, retracted more slowly, than the vulcanizates from the ethyl acrylate-chloropropyl acrylate and chloroethylvinyl ether copolymers[19].

Earlier results, obtained in a study of ethyl acrylate-allyl maleate copolymers, showed that dodecanethiol and acrylonitrile were helpful in decreasing cross-linkage. In the present study neither thiol nor acrylonitrile was noticeably beneficial in attempts to prepare soluble diene copolymers.

The vulcanizates obtained from the butadiene copolymers had tensile strengths of 1100 to 1300 lbs. per sq. in. but the ultimate elongation was slightly under 300 per cent (Table 3).

TABLE 3

VULCANIZATION* OF DIENE—ETHYL ACRYLATE COPOLYMERS

(Preparation described in Table 2)

Copolymer no.		Curing time at 298° F (min.)	Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Shore A hardness	Brittle point (° C)
E31	Butadiene	180	1280	270	61	..
E32	Butadiene	120	1240	290	60	..
E33	Butadiene	120	1160	280	62	..
D45	Isoprene	120	630	730	49	−15
D46	Isoprene	120	1130	680	55	−11
D47	Isoprene	120	990	750	58	− 9
D48	Isoprene	120	1200	370	66	− 7
D49	Isoprene	60	1190	210	65	− 4
D47	Isoprene	180	1190	550	60	−10
D125	Isoprene	180	840	560	54	..
D50	Piperylene	60	820	780	48	−18
D51	Piperylene	180	1110	910	58	− 8
D52	Piperylene	120	510	1020	60	− 8
D53	Piperylene	60	670	640	62	− 8
D81	Piperylene	120	1020	590	62	− 6
D82	Piperylene	60	920	770	55	− 4
D83	Piperylene	60	940	830	50	..
E18	2,3 Dimethylbutadiene	240	930	530	53	..
E19	2,3 Dimethylbutadiene	240	1310	450	62	..

* Recipe: copolymer, 100; 2-mercaptobenzothiazole, 0.5; zinc oxide, 5; stearic acid, 2; sulfur, 2; tetramethylthiuram disulfide, 1; and SRF carbon black, 30.

Isoprene copolymers.—Most of the isoprene vulcanizates had slightly lower tensile strengths, but much higher elongations than the butadiene vulcanizates (Table 3). This fact and the higher boiling point of isoprene made this diene appear more attractive than butadiene as a copolymerizing monomer.

Isoprene copolymers were vulcanized successfully with (1) sulfur with various accelerators, (2) quinone dioxime and red lead, (3) benzoyl peroxide with various reinforcing agents, and (4) sulfur with litharge (Table 4). The results show that a variety of curing[20] and reinforcing agents can be used to produce different types of vulcanizate. Harder and stronger vulcanizates were obtained by using larger proportions of Furnex beads or a harder black (Micronex). Both zinc oxide and calcium carbonate (Kalvan) were employed satisfactorily as reinforcing agents in the absence of carbon black.

The isoprene-ethyl acrylate copolymer was blended with both Butyl rubber[21] and Paraplex-× 100[22] and the blends were satisfactorily vulcanized, both with sulfur and accelerators and with benzoyl peroxide (Table 5). The vulcanizates containing either Butyl rubber or Paraplex-× 100 (rubbery polyester) had lower brittle points than the vulcanizates made entirely from the isoprene copolymer.

The general effect of using methyl acrylate instead of the ethyl ester in preparing the isoprene copolymers was to increase the tensile strength, hardness, and brittle point (Table 6). The vulcanizate from the copolymer made of 92 per cent methyl acrylate, 6 per cent acrylonitrile, and 2 per cent isoprene had a tensile strength and elongation of 1720 lbs. per sq. in. and 500 per cent,

TABLE 4

VULCANIZATION OF ISOPRENE-ETHYL ACRYLATE COPOLYMER WITH VARIOUS RECIPES*

	Parts per 100 parts of copolymer														
Expt. no.	Captax	Zinc oxide	Stearic acid	Sulfur	Furnex beads	Micronex beads	Tuads	Red lead	Quinone dioxime	Other agents	Curing time at 298° F (min.)	Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Shore A hardness	Brittle point (° C)
933	0	5	3	0	60	0	0	10	2		180	2160	140	86	
934	0.5	5	2	2	30	0	1	0	0		180	1190	550	60	−10
937	0.5	5	2	2	0	30	1	0	0	0.35, Rodo 0	120	1230	420	71	
938	0.5	5	2	2	0	30	1	0	0	0.35, Rodo 10	60	1270	480	68	
939	0.5	5	2	2	0	30	1	0	0	0.35, Rodo 0; 0.35, Rodo-10	60	1160	500	68	
940	0	0	0	0	0	0	0	0	0	150 Iron oxide; 5 Luperco-A	20†	1030	460	61	
953	0.5	5	2	2	30	0	0	0	0	1, Butesan	240	1120	490	57	
954	0.5	5	2	2	20	0	1	0	0	20, Kalvan	120	1060	570	60	
987	0	0	0	0	0	0	0	0	0	100, Iron oxide; 5 Luperco-A	20†	250	870	45	
988	0.5	50	2	2	0	0	1	0	0		240	1230	320	82	
989	0.5	5	2	2	0	0	1	0	0	40, Kalvan	180	1000	760	54	
1037	0.5	5	2	2	30	0	0	0	0	2, Santocure	120	830	610	51	
1038	0.5	5	2	3	30	0	0	0	0	2, R-2 crystals	180	940	670	55	
1039	0.5	5	3	1.5	30	0	0.75	0	0	0.75, Selenac	180	1160	520	50	
1040	0	5	2	1.5	30	0	1	0.5	0	1.5, Selenac	90	810	530	49	− 8
1041	0	0	0	3	30	0	0	0	0	5, Litharge	120	590	880	35	−10
1046	0	5	2	2	30	0	1	0	0	0.5, Rotax	180	1090	540	52	− 9
1043	0.5	5	2	2	30	0	1	0	0		180	840	560	54	− 7
1053	0	0	0	0	0	0	0	0	0	5, Luperco-A; 125, Rayox	10	220	860	39	
1054	0	0	0	0	0	0	0	0	0	5, Luperco-A; 125, Raycal	40	180	610	44	

* Copolymer used in the 900 series experiments was prepared in Experiment D97, Table 2; that used in the 1000 series experiments was prepared in Experiment D125, Table 2.

† At 210° F.

TABLE 5

BLENDS OF ISOPRENE—ETHYL ACRYLATE COPOLYMER WITH BUTYL RUBBER* OR PARAPLEX × 100†

Expt. no.	Percentage by weight: Isoprene copolymer	Butyl rubber A	Paraplex ×100	Parts per 100 parts: Zinc oxide	Sulfur	Cure: Temp. (° F)	Min.	Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Shore A hardness	Brittle point (° C)	Tensile product
934‡	100	0	0	5	2	298	180	1190	550	60	−10	655
950‡	80	20	0	4	1.6	298	120	1060	580	55	−11	615
951‡	50	50	0	2.5	1	298	120	1040	600	55	−40	625
952‡	20	80	0	1	0.4	298	120	1840	730	53	−57	1340
1027‡	0	100	0	0	0	298	180	2340	790	41	−65	1850
1030§	100	0	0	0	0	260	10	850	330	53	− 7	280
1931§	90	0	10	0	0	260	10	880	400	58	−10	350
1932§	80	0	20	0	0	260	20	740	470	55	−17	350
1933§	65	0	35	0	0	260	20	950	420	54	−28	400
1934§	40	0	60	0	0	260	40	1170	420	60	−36	490
1035§	0	0	100	0	0	260	40	1570	370	62	−45	580

* Butyl rubber A contained 5 parts zinc oxide and 1.5 part sulfur; other ingredients were 0.5-part Captax, 2 parts stearic acid, 30 parts Micronex beads, and 1 part Tuads.

† Blend (100 parts) compounded with 4.5 parts Luperco-A and 80 parts Kalvan; Paraplex-× 100 is a polyester obtained from the Resinous Products & Chemical Co., Philadelphia.

‡ Isoprene copolymer prepared in Experiment D97, Table 2.

§ Isoprene copolymer prepared in Experiment D125, Table 2.

TABLE 6

EFFECT OF METHYL ACRYLATE ON THE PROPERTIES OF ISOPRENE-ACRYLIC ESTER VULCANIZATES*

Expt. no.	Percentage: Ethyl acrylate	Methyl acrylate	Ammonium persulfate	Temp. (° C)	Time (hours)	Yield (%)	Curing time at 298° F (min.)	Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Shore A hardness	Brittle point (° C)
D97	92	0	0.11	74–90	2.7	95	180	1190	550	60	..
D106	83	9	0.18	75–92	3.5	92	240	890	960	57	−10
D107	76	16	0.11	75–91	2.5	90	180	1290	680	61	− 8
D108	9	92	0.24	70–89	4.7	91.5	240	1720	500	96	14
D109	62	30	0.16	75–92	4.0	90	180	1310	560	62	0
D110	40	52	0.27	72–75	3.5	97.5	..	..	..	..	..
D117†	89	0	0.41	76–92	4.0	92	120	1040	290	55	..

* Monomer mixtures also contained 2% isoprene and 6% acrylonitrile; samples were prepared as 40% emulsions with 0.75% Tergitol Penetrant No. 4 as emulsifying agent. Copolymers compounded as in Table 3.

† Monomer mixture contained 3% allyl maleate.

Table 7

Vulcanization of Piperylene-Ethyl Acrylate Copolymer with Various Recipes*

Expt. no.	Parts per 100 parts of copolymer								Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Shore A hardness
	Captax	Stearic acid	Sulfur	Red lead	Quinone dioxime	Furnex beads	Tuads	Zinc oxide			
893	0.5	2	2	0	0	30	1	5	1020	590	62
894	0	3	0	10	2	60	0	5	1460	310	83
899	0	3	0	10	2	30	0	5	910	420	57
900	0	3	0	10	2	45	0	5	1340	380	73

* The piperylene copolymer was prepared in Experiment D81, Table 2; samples were cured for two hours at 298° F.

Table 8

Copolymers of 2,3-Dimethylbutadiene-1,3 and Ethyl Acrylate*

Expt. no.	2,3-Dimethyl-1,3-butadiene (%)	Acrylonitrile (%)	Ammonium persulfate (% of monomer)	Time (hours)	Yield (%)	Intrinsic viscosity of copolymer†	Curing time at 298° F (hours)	Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Shore A hardness
E110	2.6	6	0.043	1.0	96	1.38	2	1340	590	65
E111	5.2	6	0.060	2.0	94	1.10	2	1080	520	70
E135‡	4.6	..	....	3.3	75	....	2	350	430	63
E136	4.6	..	0.015	1.0	95	....	3	1140	310	62
E137	10.0	..	0.012	2.5	90	....	3	1340	180	68
E138	15.0	..	0.019	2.2	70	....	1	1190	260	68
E159	5.0	..	0.010	3.5	94	1.97	2	1020	310	60
E160	2.0	..	0.012	4.0	81	2.49	2	1080	580	55
E161	10.0	5	0.048	5.5	94	1.22	2	1120	230	62
E162	10.0	..	0.025	3.5	100	Insol.	2	960	200	62
E163	2.0	5	0.028	3.0	99	2.70	2	1320	460	56
E164	5.0	5	0.025	3.0	92	1.73	2	1160	390	63
E191	2.0	..	0.012	2.0	89	....	2	950	510	49

* Samples prepared in emulsion (33%) with 0.75% Tergitol Penetrant No. 4 emulsifying agent; vulcanization recipe; copolymer, 100 parts; 2-mercapto benzothiazole, 0.5-part; zinc oxide, 5 parts; stearic acid, 2 parts; sulfur, 2 parts; tetramethylthiuram disulfide, 1 part; and SRF carbon black, 30 parts.

† Calculated as $\frac{\ln \eta_r}{c}$.

‡ Succinic acid peroxide, 0.033%.

TABLE 9

EMULSION POLYMERIZATION OF MISCELLANEOUS DIENE-ETHYL ACRYLATE MIXTURES

Expt. no.	Diene	Percentage						Temp. (° C)	Time (hours)	Yield (%)
			Acrylonitrile	Dodecanethiol	Ammonium persulfate	Tergitol penetrant no. 4	Solids			
D58	Cyclopentadiene	2.1	6.0	....	0.04	0.75	25	82–92	1.7	94
D74	Myrcene	2.1	....	....	0.08	0.75	25	82–92	0.8	89
D75	Myrcene	2.1	6.0	....	0.08	0.75	25	82–92	1.0	88
D76	Myrcene	2.1	6.0	0.10	0.08	0.75	25	82–92	1.0	89
D78	Alloöcimene	2.1	....	....	1.18	0.75	25	82–92	Did not polymerize	
D89	Divinylbenzene	4.0	....	....	0.03	0.75	25	79–91	1.7	95
D90	Divinylbenzene	4.0	6.0	....	0.03	0.75	25	70–91	3.5	92
D91	Divinylbenzene	4.0	6.0	0.10	0.03	0.75	25	78–92	2.5	93
D88	2-Methylpentadiene	2.5	6.0	....	0.77	0.75	25	82–92	8.5	Polymer very soft
E27	2-Chlorobutadiene	5.0	....	....	0.79	0.50	36	80–91	7.5	96
E48	Vinylcyclohexene	3.3	6.0	0.10	0.07	0.45	43	80–90	2	96
E190†	Piperylene	10.0	....	....	0.24	0.75	33	71–91	5.2	87.5

* Moisture-free basis.
† 1% Triton 720 (moisture-free basis) also used.

respectively. The use of allyl maleate instead of methyl acrylate, which required more catalyst in the preparation of the copolymer, seemed detrimental (Table 6, Expt. D117).

Piperyline copolymers.—The piperyline copolymers were somewhat like the isoprene copolymers in that their vulcanizates had relatively high tensile strengths and elongations. The effect of increasing the amount of carbon black was to increase the tensile strength and hardness and decrease the elongation (Table 7).

Dimethylbutadiene copolymers.—Although most of the dimethylbutadiene copolymers (Table 8) had moderately high tensile strengths and elongations, the outstanding characteristics of these copolymers were their solubility in organic solvents and the comparative ease with which these materials could be milled. Probably decreased cross-linkage was an important factor in this behavior. The viscosities of solutions containing 0.05 gram of copolymer in 100 cc. of toluene indicated that the molecular weights of the copolymers were less than those of some of the ethyl polyacrylate and the chloropropyl acrylate copolymer samples described previously[3].

Miscellaneous diene copolymers.—The other diene copolymers studied were less satisfactory than the butadiene, isoprene, piperylene and dimethylbutadiene copolymers discussed above. Cyclopentadiene, myrcene, and divinylbenzene (Table 9) apparently yielded vulcanizable copolymers, but the tensile strengths of their vulcanizates were low (Table 10).

TABLE 10

VULCANIZATION* OF MISCELLANEOUS COPOLYMERS

(Preparations described in Table 9)

Copolymer no.	Curing time at 298° F (min.)	Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Shore A hardness	Brittle point (° C)
D58	180	490	1540	45	− 9
D74	180	430	310	49	−14
D75	60	810	530	52	− 6
D76	180	780	460	54	− 9
D89	180	210	1080	50	−10
D90	180	920	420	60	− 2
D91	180	560	500	60	1
E190	60	830	200	67	..

* Vulcanization recipe is given in footnote * of Table 3.
Unsatisfactory (*i.e.*, pitted) products were obtained on attempted vulcanization of copolymers E27 and E48.

Copolymerization occurred with difficulty or not at all when alloöcimene and methylpentadiene were used. Chloroprene and vinylcyclohexene gave products that could not be molded satisfactorily into test-specimens because of pitting or excessive tackiness.

ESTER COPOLYMERS

Copolymers of ethyl acrylate and allyl maleate had been studied previously[2], but methods for preparing rubbery products having high tensile strength had not been found. Since dodecanethiol and acrylonitrile were beneficial in the earlier preparation of allyl maleate copolymers, these two materials were used in some experiments of the present study (Table 11).

TABLE 11

EMULSION POLYMERIZATION OF ETHYL ACRYLATE AND POLYUNSATURATED ESTERS

Expt. no.	Polyunsaturated monomer	Percentage	Acrylonitrile	Dodecanethiol	Ammonium persulfate	Tergitol penetrant no. 4*	Solids	Time (hours)	Yield (%)
A259†	Crotyl acrylate	6.4	5	....	....	....	45	0.7	..
D38	Crotyl acrylate	4.0	..	....	0.005	0.5	25	1.7	85
D84	Crotyl acrylate	4.0	6	....	0.055	0.75	25	4.5	57
D85	Crotyl acrylate	4.0	6	0.1	0.055	0.75	25	4.5	91
D35	Cinnamyl acrylate	9.6	..	....	0.66	0.75	25	2.3	92
D36	Citronellyl acrylate	10.7	..	....	0.023	0.5	25	1.0	89
D37	Citronellyl acrylate	10.7	6	....	0.025	0.5	25	3.7	84
D40	Geranyl acrylate	3.2	..	....	0.01	0.5	25	2.5	82
D63	Geranyl acrylate	3.2	6	....	0.03	0.75	25	2.0	85
D64	Geranyl acrylate	3.2	6	0.1	0.03	0.75	25	2.0	84
D41	Furfuryl acrylate	2.4	..	....	0.03	0.50	25	2.0	79
D42	Allyl lactate maleate	5.2	..	....	0.005	0.50	25	0.7	56
D43	Allyl lactate maleate	5.2	..	....	0.01	0.50	25	0.7	72
D61	Diethylene glycol bis-(allyl carbonate)	7.5	..	....	....	0.50	25	0.7	91
D62	Diethylene glycol bis-(allyl carbonate)	7.5	6	....	....	0.50	25	1.2	93
D65	Rhodinyl acrylate	6.5	..	....	0.05	0.75	25	2.0	97
D66	Rhodinyl acrylate	6.5	6	....	0.05	0.75	25	2.5	84
D67	Rhodinyl acrylate	6.5	6	0.1	0.03	0.75	25	1.8	83
E204‡	Allyl phthalate	5.0	..	....	....	0.38	33	0.8	..
D86	Allyl maleate	3.0	3	0.1	0.0003	0.50	40	7.0	75
E10	Allyl maleate	0.1	..	....	0.022	0.50	32	1.2	94
D101	Methyl pentenyl acrylate	4.8	..	....	0.053	0.67	33	3.0	84
D101	Methyl pentenyl acrylate	4.8	6	....	0.053	0.67	33	2.5	91
D102§	Methyl pentenyl acrylate	4.8	6	0.1	0.053	0.67	33	1.8	93

* Calculated as 25% emulsifying agent.
† Triton K60, 0.5; and 0.5% of 30% hydrogen peroxide used
‡ Triton-720, 1% (calculated as 30% solids).
§ Intrinsic viscosity of polymer, 2.14.

Unlike the diene copolymerizations discussed above, the copolymerization of the polyolefinic esters with ethyl acrylate followed in general a more normal course with respect to the amount of catalyst and time of polymerization. The higher boiling points of the polyolefinic esters permitted the use of uniformly higher initial refluxing temperatures and minimized loss during the polymerization.

The crotyl and geranyl acrylate[7] copolymers yielded the best vulcanizates (Table 12, D63, D64, D84, and D85). Although the tensile strengths of their

TABLE 12

VULCANIZATION* OF ETHYL ACRYLATE AND POLYOLEFINIC ESTER COPOLYMERS

(Preparation described in Table 11)

Copolymer no.	Curing time at 298° F (hours)	Tensile strength (lbs. per sq. in.)	Ultimate elongation (%)	Shore A hardness	Brittle point (° C)
A259	0.5	1470	310	64	− 1
D38	3	1110	300	54	−14
D84	3	1200	350	60	− 5
D85	3	1220	340	59	..
D36	3	740	210	53	−14.5
D37	3	1000	230	50	−10
D40	3	1110	300	52	−19
D63	3	1310	340	58	− 7
D64	1	1380	390	53	−10
D41	3	330	370	46	−15
D42	3	510	860	49	−18
D43	3	540	230	54	−14
D65	1	580	160	54	−14
D66	2	1090	220	62	− 8
D67	2	1100	220	58	− 7
E204†	3	190	460	33	..
D86†	4	140	1070	45	..
E10‡	2	1470	640	50	..
D101†	2	0	50	75	..
D102†	2	0	60	75	..

* Vulcanization recipe is given in footnote * of Table 3.
† Stock did not vulcanize.
‡ Recipe: Copolymer, 100; red lead, 10; zinc oxide, 10; stearic acid, 3; *p*-quinone dioxime, 2; and SRF carbon black, 30.

vulcanizates were moderately high, the ultimate elongation was always less than 400 per cent. Crotyl acrylate was found in an earlier study[7] to have relatively little tendency to form cross-linked copolymers when polymerized with methyl acrylate in an ethyl acetate solution. Geranyl acrylate, however, readily formed cross-linked copolymers with methyl acrylate[7]. The cinnamyl acrylate and furfuryl acrylate copolymers were inelastic. The diethylene glycol bis-(allyl carbonate)[23] copolymer vulcanizates were not suitable for testing.

ETHYL ACRYLATE–ETHER COPOLYMERS

The only unsaturated ether copolymer that yielded a satisfactory vulcanizate was that obtained from vinyl ether (Table 13). The vinyl ether copolymer of Expt. D56, Table 13, gave a vulcanizate that was superior in combined tensile strength and ultimate elongation (1280 lbs. per sq. in. and 960 per cent) to any of the other vulcanizates obtained in the present study. The

TABLE 13

EMULSION POLYMERIZATION AND VULCANIZATION OF ETHYL ACRYLATE AND POLYOLEFINIC ETHER COPOLYMERS

Expt. no.	Polyolefinic ether	Percentage						Time (hours)	Yield (%)	Curing time at 298° F (hours)	Tensile strength (%)	Ultimate elongation (%)	Shore A hardness	Brittle point (° C)
			Acrylonitrile	Dodecanethiol	Ammonium persulfate	Tergitol penetrant no. 4†	Solids							
D55	Vinyl ether	2.1	..	....	0.01	0.75	25	0.5	96	3	380	950	41	−19
D6	Vinyl ether	2.1	6	....	0.03	0.75	25	0.7	93	3	1280	960	48	−12
D557	Vinyl ether	2.1	6	0.1	0.02	0.75	25	1.0	94	3	910	1280	47	−10
D68	Allyl ether‡	3.0	..	....	0.03	0.75	25	1.3	88	1	<100	>2400	36	..
D69	Allyl ether‡	3.0	6	....	0.03	0.75	25	1.8	98	2	<100	>2200	45	..
D103	Methallyl ether‡	4.0	..	....	0.02	0.67	38	0.8	91.5	2	<100	100	60	..
D104	Methallyl ether‡	4.0	6	....	0.074	0.67	38	2.8	93	2	<100	100	65	..
D105	Methallyl ether‡	4.0	6	0.13	0.067	0.67	38	1.0	79	2	<100	100	68	..
D77	Allyl methyl glucoside‡§	4.2	..	....	0.03	0.75	25	0.5	95	3	140	120	59	..
E16	Diallyl glycol‡	2.4	..	....	0.06	1.25	20	1.0	92	4	100	510	42	..
E17	Diallyl glycol	3.0	6	....	0.08	1.25	20	1	87	2	510	580	45	..

* Vulcanization recipe is given in footnote * of Table 3.
† Moisture-free basis.
‡ Stock did not vulcanize.
§ Approximately 3.5 allyl groups.

vinyl ether copolymers made in two subsequent experiments gave pitted vulcanizates. It has been shown that vinyl ether has little tendency to form cross-linked copolymers[24]. Nozaki[25] has published information on the copolymerization of vinyl ether.

An ethyl acrylate-allyl starch[9] copolymer, which appeared to be cross-linked, could not be compounded. The ethyl acrylate-allyl ether product was extremely soft and tacky, and its vulcanizates were badly pitted. The methallyl ether product (presumably of low molecular weight and plasticized with methallyl ether) also was unusually soft and sticky. The diallyl ether of ethylene glycol[8] seemed much more suitable for making vulcanizable acrylic resins than either allyl ether or methallyl ether (Table 13).

SUMMARY AND CONCLUSIONS

Ethyl acrylate was copolymerized with small proportions of eleven dienes, eleven polyolefinic esters, and six polyolefinic ethers in an attempt to prepare olefin-containing acrylic elastomers that would vulcanize readily, yielding products having improved rubbery characteristics. In general, the resulting copolymers were insoluble in organic solvents, presumably because of cross-linkage. Acrylonitrile and dodecanethiol appeared beneficial in the copolymerization of ethyl acrylate with polyolefinic esters, but of questionable value in the diene polymerizations.

The best vulcanizates from the standpoint of tensile strength and elongation were obtained from an ethyl acrylate-acrylonitrile-vinyl ether copolymer. Some preparations of this copolymer, however, had a tendency to pit and bubble during vulcanization.

Isoprene, piperylene, and 2,3-dimethylbutadiene were more suitable for preparing vulcanizable ethyl acrylate copolymers than the other dienes studied; their vulcanizates had moderately high tensile strengths and elongations. Some of the dimethylbutadiene-ethyl acrylate copolymers were soluble.

Crotyl acrylate and geranyl acrylate, when copolymerized with ethyl acrylate, yielded copolymers that gave vulcanizates having moderately high tensile strengths and elongations ranging from 300 to 400 per cent.

The physical properties of the vulcanizates prepared from unsaturated acrylic copolymers were not superior to those of the chloropropyl acrylate and chloroethyl vinyl ether products described previously[19].

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THE REACTION OF SULFUR AND SULFUR COMPOUNDS WITH OLEFINIC SUBSTANCES. VI. FACTORS INFLUENCING CYCLIC SULFIDE FORMATION IN THE REACTION OF SULFUR WITH POLYISOPRENES *

GEORGE F. BLOOMFIELD

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

The reaction of sulfur with polyisoprenes[1] yields ditertiary cyclic sulfides[2] in addition to intermolecularly linked polysulfides, in which an average of four sulfur atoms has become interposed between a pair of polyisoprene molecules, with an overall loss of one double bond. Although the structure of these polysulfides has not yet been ascertained with certainty, there is every reason to believe that they are alkyl-alkenyl in type, by analogy with the general mode of reaction of sulfur with olefins[1].

Prolongation of the time of reaction of sulfur with olefins always results in the formation of a certain amount of nonvolatile substances of reduced hydrogen-to-carbon ratio[3] as a result of the reaction of primarily formed polysulfides with centers of olefinic unsaturation present either in the polysulfides themselves or in the excess of olefin which is usually maintained in these reactions[4]. The loss of unsaturation resulting from these secondary reactions has been effectively demonstrated[5].

Reference has also been made[4] to the ready formation of cyclic sulfides when bis-dihydromyrcene polysulfide is heated with dihydromyrcene, and it is now established that the proportion of cyclic sulfide to intermolecular polysulfide, *i.e.*, cross-linked material, in the mixture obtained by the reaction of sulfur with dihydromyrcene varies with the time of reaction. When these reactants are heated at 141° for longer than 3 hours, only a comparatively small increase in the yield of intermolecular polysulfides results, in spite of the fact that much free sulfur is still present, and this suggests that existing cross-linkages are being converted to cyclic sulfide at a rate comparable to that in the formation of fresh cross-linkages (Table I). As the reaction proceeds further and the proportion of free sulfur present diminishes, the former rate may even exceed the latter. Even in very short reaction periods, cyclic sulfide is not entirely absent, indicating that some of the cyclic sulfide originates in the sulfur-polyisoprene reaction itself.

It follows from the foregoing discussion that any substance which increases the rate of reaction of sulfur with rubber will, by enabling a given amount of sulfur to enter into reaction in a shorter time, give a greater proportion of cross-linked polysulfide relative to cyclic sulfide, and so increase the efficiency of the sulfur as a cross-linking reagent—always provided that the auxiliary substance does not also increase the rate of reaction of the polysulfide with the

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olefin. So-called accelerators developed empirically by the rubber industry facilitate greatly the incorporation of sulfur into rubber, and recent work has shown that these substances similarly increase the rate of reaction of sulfur with olefins generally[6]. Such auxiliary substances could conceivably influence the reaction of sulfur with polyisoprenes in any of three ways: (1) by altering the relative proportions of cyclic sulfide and polysulfide, either in the manner just indicated, or by promoting a cross-linking rather than a cyclizing reaction of the sulfur[2]; (2) by influencing the average number of sulfur atoms in the cross-linkages; or (3) by influencing the unsaturation pattern adjacent to the sulfur linkage. Clearly, both (1) and (2) would affect the cross-linking efficiency of the sulfur, while the effect of (3) would be more evident in the ultimate properties of the product, *e.g.*, its oxidizability or its thermal stability. The complexity of the cross-linked sulfuration products of polyisoprenes renders these materials unsuitable for studying the effects of (2) and (3), and a study of simple monoölefins, to be reported in a subsequent paper, is more informative. There is, however, already available some indication of the positive effects which accelerators have both on the nature of the cross-linkage and on its associated unsaturation pattern. Armstrong, Little and Doak[6] observed an increase in the yield of monosulfides and a decrease in that of polysulfides when mercaptobenzothiazole was used to accelerate the reaction of sulfur with 2-methyl-2-butene. Significant differences in unsaturation value and in the nature of the reaction of methyl iodide with rubbers vulcanized in the presence of various accelerators have also been reported[7].

TABLE I

INFLUENCE OF REACTION TIME ON CROSS-LINKING EFFICIENCY IN DIHYDROMYRCENE AT 141° C

(10 parts sulfur per 100 parts hydrocarbon)

Experiment no.	Time of heating (hours)	Combined sulfur* (%)	Weight ratio**	Sulfur ratio***
1	1.5	1.4	5.6	10
2	3	3.0	4.4	8
3	6	3.8	2.9	5

* Weight of sulfur which has reacted with 100 grams of hydrocarbon.
** Ratio of weight of polysulfide to weight of cyclic sulfide.
*** Ratio of sulfur in polysulfide linkages to sulfur in intramolecular cyclic linkages.

The results presented in Table II clearly reveal that some common accelerators exert a pronounced effect on the cross-linking efficiency of sulfur with the diisoprene, dihydromyrcene.

The behavior of mercaptobenzothiazole and benzothiazoyl disulfide at first appeared to be anomalous (Experiments 5 to 10), but it was observed later that traces of nitrogenous bases of a type similar to the decomposition products of some of the naturally-occurring nitrogenous components of raw rubber[8] influence markedly (in an unknown manner) the mode of action of these particular accelerators. This behavior provides a probable explanation of the difficulties experienced by McColm and Haefele[9] and by Martin[10] in obtaining satisfactory vulcanization of highly purified rubber hydrocarbon when mercaptobenzothiazole was used as accelerator.

A further peculiarity of mercaptobenzothiazole in rubber vulcanization is that it requires the presence of a trace of water before it can exert its maximum

TABLE II

INFLUENCE OF ACCELERATORS ON CROSS-LINKING EFFICIENCY IN THE SULFUR-DIHYDROMYRCENE REACTION

(10 parts sulfur per 100 parts hydrocarbon)

Expt. no.	Accelerator	Auxiliary substances*	Time (min.)	Temp. (° C)	Combined sulfur (%)	Weight ratio	Sulfur ratio	Transformation products of accelerators
5	MBT	—	30	141°	1.7	1.6	3	
6	MBT	1	30	141	2.8	2.2	4	
7	MBT	1, 3	30	141	1.6	1.8	3	Zinc salt of MBT and MBTS
9	MBT	1, 2	30	141	3.0	5.0	9	
10	MBT	2	30	141	4.2	2.5	4.5	
14	MBT	1, 2, 4	30	141	2.3	7	12	
12	MBTS	1, 2	30	141	0.3	—	—	Reaction insignificant
15	MBTS	1, 2, 4	30	141	2.4	9.3	15	
16	DPG	1, 2	45	141	2.0	>40	>80	Complex polysulfide
18	ZDC	—	15	141	2.4	4.9	7.5	
19	ZDC	—	60	100	2.0	6	10	
20	TMT	1, 2	20	141	2.2	5.5	13	Zinc dimethyldithiocarbamate

* Auxiliary substances (see Experimental Section) as follows: 1, zinc oxide; 2, zinc propionate; 3, stearic acid; 4, tetramethylammonium stearate.

effect in increasing the cross-linking efficiency of sulfur (Table III). This effect is reflected in the proportion of zinc sulfide formed from the zinc oxide always used in conjunction with this accelerator; it has been suggested[12] that the zinc sulfide formed provides a measure of the degree of cross-linking.

Nitrogenous accelerators of the diphenylguanidine type appear to suppress altogether the formation of cyclic sulfide. It is perhaps significant that these substances also catalyze the conversion of thiols (which have been postulated as intermediates in cyclic sulfide formation[2]) to polysulfides in the presence of sulfur[13], and are capable of bringing rapidly into solution the insoluble modification of sulfur present in flowers of sulfur[14].

An example has been included in this paper of an accelerator, tetramethylthiuram disulfide, which is capable of effecting cross-linking in the absence of elementary sulfur, since it has been obscure whether this substance functions by promoting carbon-carbon cross-linkages[15] or by liberating a reactive form of sulfur[16]. It has long been known that tetramethylthiuram disulfide decomposes at temperatures above 100° C, giving tetramethylthiourea, carbon disulfide, and sulfur[17], and the rate of this decomposition (see below) is appreciably increased in the presence of rubber hydrocarbon. In the presence of zinc

TABLE III

INFLUENCE OF MOISTURE ON MERCAPTOBENZOTHIAZOLE ACCELERATED VULCANIZATION

Conditioning of sample	Cure at 141° C (min.)	Combined sulfur (%)	Sulfur as ZnS (%)	Swelling index* (Q_m)
Dry	20	0.75	.002	6.2
Wet	20	1.7	.041	4.5
Dry	45	1.7	.024	5.0
Wet	45	2.05	.075	4.5
Dry	90	2.05	.062	4.8
Wet	90	2.6	.141	4.1

* For the influence significance of Q_m as a quantitative indication of the degree of cross-linking, see Gee[12].

oxide, normally used in admixture with tetramethylthiuram disulfide in the so-called "sulfurless" vulcanization of rubber, the formation of zinc dimethyldithiocarbamate has also been observed[18].

In its reaction with dihydromyrcene in the presence of zinc oxide, tetramethylthiuram disulfide is now shown to give a reaction product easily separable into two distinct fractions. One of these (not necessarily homogeneous) contains only carbon, hydrogen and sulfur, the latter in proportion too great for a monosulfide and too low for a disulfide; there is also some H/C deficiency. The other fraction contains both nitrogen and sulfur, and its composition indicates combination of a $Me_2N \cdot C \cdot S$— fragment with a dihydromyrcene molecule. The formation of these reaction products is in conformity with the usual finding of 0.4 to 0.5 per cent of combined sulfur in rubbers vulcanized with tetramethylthiuram disulfide. Both tetramethylthiuram monosulfide and zinc dimethyldithiocarbamate are separable from the dihydromyrcene reaction products; both have been isolated from the corresponding rubber-thiuram vulcanizates[19]. Tetramethylthiuram disulfide is thus seen to function as a sulfur-liberating agent, giving both mono- and disulfide cross-linkages; cyclic sulfide formation is negligible. Carbon-carbon cross-linking is not entirely excluded as a subsidiary reaction mechanism, but it is apparently not the principal mode of cross-linking.

EXPERIMENTAL PART

(Microanalyses were carried out by W. T. Chambers and Miss E. Farquar.)

Procedure.—The hydrocarbon, sulfur, and other ingredients were heated together in an oil bath thermostatically controlled at 141° ± 0.2° C, with stirring, in an atmosphere of purified nitrogen. The reaction mixture was left overnight at 0° C, then cooled to −20° C to crystallize out as much free sulfur as possible, and filtered rapidly. The filtrate was fractionally distilled, and all volatile fractions (at 1 mm.) were analyzed for sulfur to obtain an overall yield of cyclic sulfide, since dihydromyrcene and its cyclic sulfide are not readily separable. When soluble accelerator-transformation products or stearic acid were present, a benzene solution of the nonvolatile portion was passed through an alumina column, it having been found that hydrocarbon solvents elute dihydromyrcene polysulfides almost quantitatively in unchanged condition. A small portion (about 0.2 gram) of the eluted polysulfide was treated with aqueous sodium sulfite at 100° C for 2 hours; the sulfur so removed gives an approximate estimate of the free sulfur present, since the amount of polysulfide sulfur removed from dihydromyrcene polysulfide under these conditions is not large and is known with reasonable certainty[14]. The composition and yield of polysulfide observed were then corrected for the amount of free sulfur present.

Experiments 1 to 3 (*Table I*).—Dihydromyrcene (50 g.) and sulfur (5 g.) in 1.5, 3 and 6 hours at 141° C yielded, respectively, 0.34, 0.91, and 1.66 g. of cyclic sulfide, together with 1.9, 4.0, and 4.8 g. of polysulfide (found: C, 57.8; H, 8.3; S, 33.9%). When zinc oxide (2.5 g., Experiment 4) was also present, the respective yields in 3 hours were 2.1 g. of cyclic sulfide and 6.4 g. of polysulfide (found: C, 67.15; H, 9.85; S, 23.0%).

Experiments 5 to 11 and 14. (Mercaptobenzothiazole acceleration).—Experimental details are given below in tabular form, each experiment being run for 30 minutes at 141° C.

Experiments 12 and 15. (Benzothiazoyl disulfide acceleration).—Dihydromyrcene (50 g.), sulfur (5 g.), zinc oxide (2.5 g.), zinc propionate (0.25 g.), and benzothiazoyl disulfide (1 g.), heated for 30 minutes at 141° C, yielded less than 0.5 g. of reaction product after removal of unchanged hydrocarbon. The addition of 0.2 g. of benzoyl peroxide before heating gave the same result. When 0.5 g. of tetramethylammonium stearate was added, 0.37 g. of cyclic sulfide and 3.45 g. of polysulfide.

Experiments 16 and 17. (Diphenylguanidine acceleration).—Dihydromyrcene (50 g.), sulfur (5 g.), zinc oxide (2.5 g.), zinc propionate (0.25 g.), and diphenylguanidine (0.5 g.), heated for 45 minutes at 141° C yielded only a trace of cyclic sulfide, but gave 3.9 g. of polysulfide (found: C, 60.5; H, 9.0; S, 30.5). Decreasing the sulfur content to 2 g. reduced the yield of polysulfide to 2.2 g. In both experiments, 0.7 g. of zinc sulfide was formed.

Experiments 18 and 19. (Zinc diethyldithiocarbamate acceleration).—Dihydromyrcene (50 g.), sulfur (5 g.), zinc oxide (2.5 g.), and zinc diethyldithiocarbamate (0.25 g.) yielded, after 15 minutes at 141° C, 0.73 g. of cyclic sulfide and 3.6 g. of polysulfide (found: C, 62.35; H, 9.15; S, 28.45). When heated for a longer period (1 hour) at a lower temperature (100° C), the yields were 0.54 g. of cyclic sulfide and 2.9 g. of polysulfide.

TABLE IV

Experiment no.	5	6	7	8	9	10	11	13	14
Dihydromyrcene	50	50	50	50	50	50	100	50	50
Sulfur	5	5	5	5	5	5	3	5	5
Zinc oxide	—	2.5	2.5	2.5	2.5	—	5	2.5	2.5
Stearic acid	—	—	0.5	0.5	—	—	—	—	—
Zinc propionate	—	—	—	—	0.25	0.25	0.5	0.25	0.25
Mercaptobenzothiazole	1	1	1	0.25	1	1	1	—	1
Tetramethylammonium stearate	—	—	—	—	—	—	—	0.5	0.5
Yield cyclic sulfide (g.)	1.25	1.65	1.7	1.07	0.9	2.1	0.2	0.2	0.46
Yield polysulfide (g.)	2.0	3.7	3.5*	1.9	4.4	5.2	1.0	1.3	3.25

* Found: C, 59.0; H, 8.7; S, 32.3.
0.33 g. of zinc sulfide was formed in Experiment 9.

Experiment 20. (Tetramethylthiuram disulfide acceleration).—Dihydromyrcene (50 g.), sulfur (5 g.), zinc oxide (2.5 g.), zinc propionate (0.25 g.), and tetramethylthiuram disulfide (0.25 g.), heated for 20 minutes at 141° C, yielded 0.4 g. of cyclic sulfide and 3.25 g. of polysulfide (found: C, 60.5; H, 8.7; N, 0; S, 30.8).

Experiment 21. (Reaction of tetramethylthiuram disulfide with dihydromyrcene).—Dihydromyrcene (50 g.), zinc oxide (2.5 g.), zinc propionate (0.25 g.), and tetramethylthiuram disulfide (1.5 g.) were heated together for 30 minutes at 141° C. On cooling, a yellow crystalline substance separated. The mixture was frozen as in previous experiments, and the filtered solids were extracted successively with benzene and acetone. The benzene extract yielded intensely yellow tetramethylthiuram monosulfide, m.p. 102–3° (mixed m.p. 103° with authentic specimen), together with zinc dimethyldithiocarbamate, m.p. 243° (mixed m.p. 243° with authentic specimen). The acetone extract yielded only zinc dimethyldithiocarbamate. Distillation of the filtered reaction product yielded less than 0.1 g. of cyclic sulfide, together with 1.5 g. of a nonvolatile oil, which was separated by passage through alumina into two components, eluted, respectively, with benzene and with benzene containing 1 per cent ethanol. The former was a colorless oil (0.6 g.) (found: C, 74.3;

H, 10.8; N, 0; S, 14.4; Zn, 0) and the latter was a brown gum (1.0 g.) (found: C, 56.8; H, 8.6; N, 5.2; S, 28.1; Zn, 0).

Thermal decomposition of tetramethylthiuram disulfide.—The sample (0.1 g.) was heated in a reaction vessel of the type described by Bolland[20] for determining active hydrogen. The liberation of carbon disulfide was followed by measurement of its vapor pressure, and also colorimetrically by condensing it into a piperidine-copper oleate reagent[21]. The latter method confirmed the reliability of the vapor pressure measurements. The amount of carbon disulfide evolved per minute at 140° C was 0.4 per cent of that theoretically available; in 1 hour 30 per cent of the theoretical carbon disulfide had been liberated. At 100° C, only 0.03 per cent of the theoretical carbon disulfide had been liberated in 1 hour. Yet in the presence of rubber (0.35 g. of rubber with 0.0177 g. of accelerator, deposited from a solution) 4 per cent of the theoretically available carbon disulfide was liberated in 1 hour at 100° C, and 40 per cent in 1 hour at 140° C (found: S combined with rubber, 0.5 per cent). In the presence of the rubber a trace of hydrogen sulfide was formed, and the measured vapor pressure of the carbon disulfide was suitably corrected. To ascertain the amount of hydrogen sulfide formed, the evolved gases were condensed into methylmagnesium iodide, and the hydrogen sulfide was estimated as methane.

Influence of water on mercaptobenzothiazole acceleration (*Table III*).—Samples of a rubber mix (rubber 100, sulfur 3, zinc oxide 5, stearic acid 1, MPC black 30, and mercaptobenzothiazole 0.75) were, respectively, dried over calcium chloride, or suspended in air saturated with water vapor at 15–20° C for a period of 4 weeks. Portions were subsequently press-cured, according to standard practice, at 141° C.

SUMMARY

Cyclic sulfides are to a large extent secondary products of the reaction of primarily formed intermolecular polysulfides with polyisoprene hydrocarbon, and undue prolongation of the time of reaction of sulfur with polyisoprenes favors cyclic sulfide formation and so reduces the cross-linking efficiency of the sulfur. Various accelerating substances markedly increase the cross-linking efficiency, either by permitting shorter reaction times, or by promoting a cross-linking rather than a cyclizing reaction of the sulfur. Thiuram disulfide accelerators in the absence of sulfur bring about cross-linking, the linkages being of —C—S—C type rather than C—C.

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FRACTIONATION OF PURIFIED HEVEA RUBBER *

G. T. VERGHESE

QUILON, TRAVANCORE, INDIA

INTRODUCTION

Resolution of high polymers into fractions of different molecular weights has proved to be of great value in the study of the fundamental properties of polymers. Such fractionation is generally effected by fractional adsorption[1], fractional precipitation[2], or fractional solution[3]. Of these, the last two methods have been largely used for the fractionation of rubber.

Hauser and coworkers[4] prepared a series of fractions from smoked sheet, while Bloomfield and Farmer[5] obtained different fractions from crepe rubber and partially purified latex rubber. There are no data available on the fractionation of highly purified rubber. An investigation was, therefore, undertaken to obtain a series of fractions from purified rubber hydrocarbon prepared by a method described in an earlier paper[6], and to compare the molecular weights of these rubber fractions with the molecular weights of the corresponding fractions of unpurified rubber.

Fractionation was effected by progressively dissolving out rubber in *n*-hexane containing 10 per cent methyl alcohol. Kemp and Peters[7], and also Gauser and colleagues[4], used *n*-hexane alone for fractionation. These authors pointed out that *n*-hexane is a poor solvent for rubber and would give a more efficient fractionation, but Kemp and Peters[8] observed later that the addition of polar substances like acetone or alcohol to *n*-hexane makes it a more efficient solvent, and Gee[9] found the same effect by the addition of 10 to 15 per cent of methyl alcohol to the hexane.

For purposes of comparison, unpurified rubber latex was solubilized in *n*-hexane as in the case of purified latex[6], and the rubber was then precipitated from the uncentrifuged solution by adding acetone. The analysis of these unpurified and purified rubbers is indicated below:

	Unpurified rubber (per cent)	Purified rubber (per cent)
Nitrogen	0.389	0.013
Ash	0.657	0.024

The molecular weights of the rubber fractions were determined by viscosity measurements. The fractions were dissolved in benzene or benzene-methyl alcohol mixture, as the case may be, and the viscosities of these solutions were measured by means of an Ostwald viscometer.

In the calculation of molecular weights the method described by Gee[9] was employed. It is based on the equation:

$$\eta\, sp = K_m c M$$

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 24, No. 6, pages 274–279, April 1949.

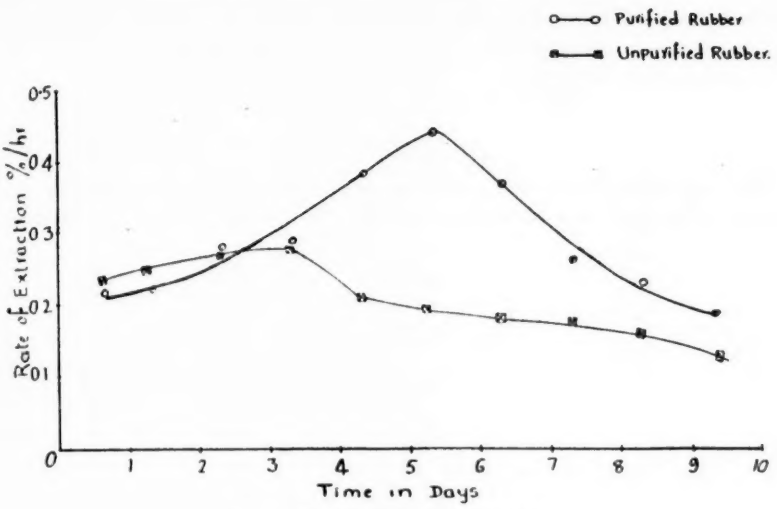

FIG. 1.—Fractional dissolution of rubber.

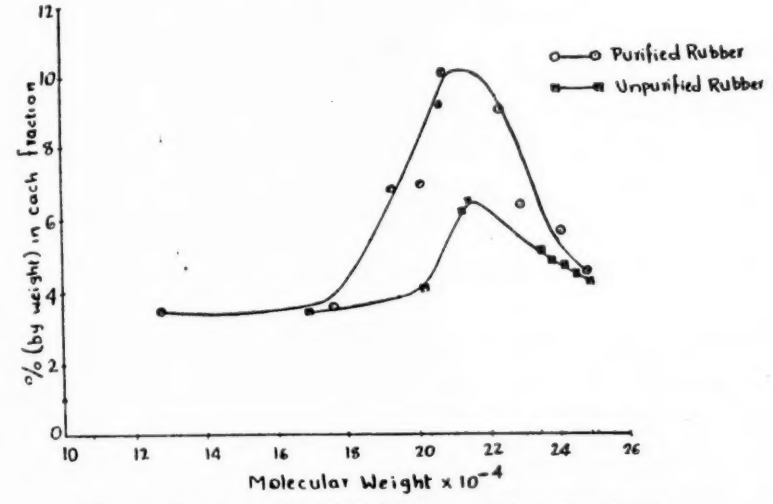

FIG. 2.—Molecular-weight distribution curves soluble fractions of rubber.

As mentioned by Gee, η_r of the solution is measured at different concentrations, and then the intrinsic viscosity $[\eta]$ is calculated from the equation:

$$[\eta] = \frac{1}{c} \log_e \eta_r$$

$[\eta]$ is then plotted against c (concentration expressed in g. per 100 cc. of the solution), and the graph extrapolated to zero concentration to obtain the limiting value, $[\eta]_o$, of intrinsic viscosity. Then:

$$M + K[\eta]_o$$

Gee has given the following values for K:

Benzene	6.0×10^4
Benzene + 15 per cent methyl alcohol	10.2×10^4

EXPERIMENTAL

The apparatus used for fractionation is illustrated in the accompanying diagram (Figure 3) and consists of a 6-liter 3-necked flask (A), provided with

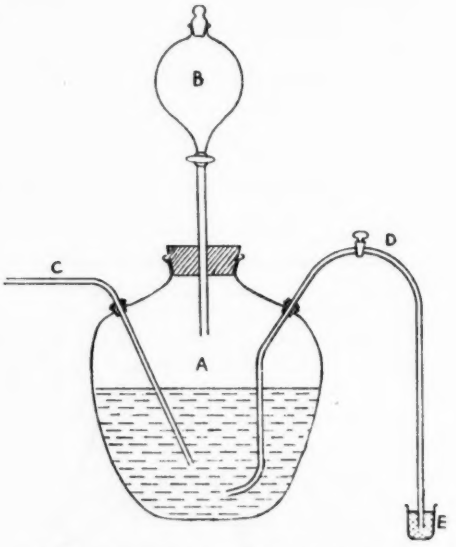

FIG. 3.—Apparatus for fractionation of rubber.

a dropping funnel (B) used for running in the solvent, and fitted with an inlet tube (C) for nitrogen, and an outlet tube (D) dipping into mercury contained in a small beaker (E). The outlet tube was used to syphon out the solution from the flask at required intervals. All the joints were made air-tight.

Cylinder nitrogen was purified by passing through a series of wash bottles containing alkaline pyrogallol, then through a sulfuric acid wash bottle, and finally through a calcium chloride tower.

The air in the apparatus was first washed out by a current of nitrogen. Also, nitrogen was drawn through all solvents before use. The fractionation was conducted in a semidark room and at room temperature.

About 20 grams of rubber were used for each fractionation. One liter of *n*-hexane containing 100 cc. of methyl alcohol was introduced into the flask, and the extraction was allowed to continue undisturbed for the required interval of time. The solvent mixture was replaced after two successive periods of 16 hours, and then after every 24 hours. The extracted rubber solution was syphoned out each time, and the rubber precipitated by adding acetone. The precipitated rubber was dried, under vacuum, in a desiccator protected from light. Ten fractions were thus obtained. The residue was dried in the same manner. The results of a typical fractionation are given in Table 1.

TABLE 1

FRACTIONATION OF PURIFIED RUBBER

Weight of rubber fractionated 20.112 g.
Molecular weight of whole rubber 34.8×10^4

Fraction	Period of extraction (hours) cumulative	Weight of fraction (g.)	Percentage extracted		Rate of extraction (% per hr.)	Molecular weight ($\times 10^4$)
			Batch	Cumulative		
I	16	0.695	3.46	—	0.21	12.7
II	32	0.710	3.53	6.99	0.22	17.6
III	56	1.373	6.83	13.82	0.28	19.3
IV	80	1.387	6.90	20.72	0.29	20.1
V	104	1.846	9.18	29.90	0.38	20.6
VI	128	2.023	10.06	39.96	0.44	20.8
VII	152	1.791	8.91	48.87	0.37	22.4
VIII	176	1.279	6.36	55.23	0.26	22.9
IX	200	1.130	5.62	60.85	0.23	24.0
X	224	0.911	4.53	65.38	0.19	24.8
Residue	—	5.914	29.41	94.79	—	Undetermined
Loss	—	1.053	5.24	100.03	—	—

TABLE 2

FRACTIONATION OF UNPURIFIED RUBBER

Weight of rubber fractionated 20.055 g.
Molecular weight of whole rubber Undetermined

Fraction	Period of extraction (hours) cumulative	Weight of fraction (g.)	Percentage extracted		Rate of extraction (% per hr.)	Molecular weight ($\times 10^4$)
			Batch	Cumulative		
I	16	0.728	3.63	—	0.23	17.0
II	32	0.784	3.91	7.54	0.24	20.2
III	56	1.179	5.88	13.42	0.25	21.2
IV	80	1.227	6.13	19.55	0.26	21.6
V	104	0.982	4.89	24.44	0.20	23.4
VI	128	0.941	4.69	29.13	0.19	23.8
VII	152	0.875	4.36	33.49	0.18	24.2
VIII	176	0.851	4.24	37.73	0.18	24.3
IX	200	0.821	4.09	41.82	0.17	25.2
X	224	0.702	3.49	45.31	0.15	26.1
Residue	—	10.224	50.94	96.25	—	Undetermined
Loss	—	0.751	3.74	99.99	—	—

The results obtained for a fractionation of unpurified rubber are given in Table 2.

DETERMINATION OF MOLECULAR WEIGHTS

The different fractions of rubber were used as soon as possible after their preparation for viscosity measurements. For the measurements of purified rubber benzene was used as the solvent for the first seven fractions, and benzene-methyl alcohol mixture for the last three fractions, as well as for the whole rubber; the case of unpurified rubber benzene was used for the first six fractions, and the mixed solvent for the last four fractions.

The concentration of the rubber solution ranged from about 0.1 to 0.01 per cent. Starting with the solution of maximum concentration, the solutions of lower concentrations were obtained by dilution with the proper solvent.

The concentration of the solution (reckoned as g. per 100 cc.) was determined as follows.

100 cc. of the solution were measured out from a burette into a weighed beaker. The solution was then evaporated, and dried to constant weight at a temperature of 40° to 50° C. During drying, the rubber was protected from light.

The viscometer containing 10 cc. of the solution was allowed to remain in a thermostat maintained at 25° C for about 15 minutes before the readings were taken. The time of flow of the solution was measured by a stop-watch reading to the fifth of a second. For each concentration a series of 5 to 6 readings was taken, and their average noted.

From the observed times of flow the relative viscosity of the solution, and from these the limiting intrinsic viscosities, and the molecular weights were calculated by the method referred to above.

The molecular weights of the soluble fractions of purified rubber are given in Table 1, and those of the corresponding fractions of unpurified rubber are given in Table 2.

DISCUSSION

Figure 1 shows that the rate of extraction of purified rubber passes through a clear maximum corresponding to an extraction period of $5\frac{1}{2}$ days.

The molecular weight distribution curves of the soluble fractions of purified and unpurified rubber are given in Figure 2.

For the unpurified rubber the molecular weight of each fraction is slightly higher than the molecular weight of the corresponding fraction of purified rubber. It appears that the process of removing the nonrubber components has modified the molecular structure in such a way as to make the molecules go into solution more readily.

In unpurified rubber only 50 per cent of the rubber undergoes fractionation compared to 70 per cent of the purified rubber. This difference does not appear to be the result of gel-sol conversion due to oxidation of purified rubber as suggested by previous workers[10]. All possible precautions were taken to minimize the effects of oxidation, and the fractionation of both purified and unpurified rubber was conducted under identical conditions. Hence the greater solubility of purified rubber may require some other explanation.

Bary[11] has suggested that gel rubber is a rubber protein combination. In the fractionation experiments in the present work a high proportion of protein was found to be present in the insoluble residue. The figures obtained for the analysis of the residues of both purified and unpurified rubber are given below.

	Purified rubber (per cent)	Unpurified rubber (per cent)
Nitrogen	0.072	0.703
Ash	0.039	0.709

The proteins and probably other impurities with which the rubber is associated may influence the solubility of rubber in the same way as carbon black affects the solubility of rubber. Obviously, the unpurified rubber used for fractionation contains an appreciable amount of protein and other impurities, whereas the purified rubber contains only minute traces of these nonrubber substances. These substances may increase the cohesive forces with which the rubber molecules are held together. These linkages resist the separation of the molecules from one another, thus preventing the rubber from going into solution.

ACKNOWLEDGMENT

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BEHAVIOR OF DIFFERENT FRACTIONS OF PURIFIED HEVEA RUBBER DURING VULCANIZATION *

G. T. VERGHESE

QUILON, TRAVANCORE, INDIA

INTRODUCTION

Considerable data on the vulcanization characteristics of molecular fractions of ordinary (unpurified) natural rubber[1] are available. There is, on the other hand, little information of any systematic work on the vulcanization of purified rubber and of its fractions.

Pummerer and Pahl[2] vulcanized the sol and gel fractions obtained from purified *Hevea* rubber, and also the purified whole rubber. But apart from a statement that whole rubber vulcanized much faster than the two fractions obtained from it, no details have been published. Vulcanization of purified whole rubber and of its sol and gel fractions was studied also by Smith and Holt[3]. They concluded that the difference which they observed in the stress-strain behavior of the fractions and whole rubber was due to differences in the rubber which persisted through vulcanization.

The present paper deals with a study of the vulcanization characteristics of different fractions of purified rubber prepared by a method described in a previous paper[4]. Also, for comparative purposes a similar study was made of the corresponding fractions of unpurified rubber.

As the difference in molecular weight of some of the fractions obtained by the above method was rather small, a grouping of the fractions was made as follows:

Purified rubber.

Group I Fractions	I–III	Average mol. wt. 16.6×10^4
Group II Fractions	IV–VI	Average mol. wt. 20.5×10^4
Group III Fractions	VII–X	Average mol. wt. 23.5×10^4
Group IV Residue		Molecular weight not determined
Also, whole rubber		Average mol. wt. 34.8×10^4

Unpurified rubber.

Group I Fractions	I–III	Average mol. wt. 19.5×10^4
Group II Fractions	IV–VI	Average mol. wt. 22.9×10^4
Group III Fractions	VII–X	Average mol. wt. 24.9×10^4
Group IV Residue		Molecular weight not determined
Also, whole rubber		Molecular weight not determined

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 24, No. 6, pages 280–283, April 1949.

The behavior of these groups of rubber on vulcanization was studied under the three following mixes:

(1) *Rubber-sulfur mix*

Rubber	100
Sulfur	10

Vulcanized at 148° C for different periods of time

(2) *Accelerated pure-gum mix*

Rubber	100
Zinc oxide	5
Sulfur	3
Stearic acid	2
Mercaptobenzothiazole	1

Vulcanized at 134° C for different periods of time

(3) *Tire tread mix*

Rubber	100
Carbon black (Micronex)	50
Zinc oxide	5
Sulfur	3
Stearic acid	7
Mercaptobenzothiazole	1

Vulcanized at 134° C for different periods of time

EXPERIMENTAL

A micro mill was used for compounding the rubber, and the Schopper rings for tensile tests were molded directly. The rings were cured in a steam-heated platen press provided with automatic temperature control. On the average, three rings were prepared and tested for each cure.

After measuring the tensile strength, the broken rings were used for the determination of combined sulfur by the method recommended by the British Standards Institution[5].

Tables 1–3 give the results obtained for the different fractions of both purified and unpurified rubber.

DISCUSSION

In the accelerated pure-gum mix both of the purified and unpurified rubber, there is not any appreciable difference in tensile strength between the whole rubber and the other fractions. In the retread mix, however, purified whole rubber shows a higher tensile strength than the other fractions for corresponding cures. The tensile strength of Group IV of unpurified rubber in this mix is higher than that of any other fraction.

Group I of purified rubber represents the purest rubber hydrocarbon in this series of investigations, and a good vulcanizate could not be obtained from this fraction in the rubber-sulfur mix, even after a 120 minutes' cure. Although corresponding to this cure it had a combined sulfur of 3.8 per cent, the vulcanizate was still plastic. On the assumption that tensile properties depend to a considerable extent on the presence of cross-links in the vulcanizate, it must be pointed out that only a portion of the sulfur that combines with the rubber

TABLE 1

RUBBER-SULFUR MIX

(Vulcanized at 148° C)

(i)	(ii)	(iii) Purified rubber					(iv) Unpurified rubber				
		Vulcanization (min.)					Vulcanization (min.)				
Property	Fraction and average molecular weight × 10^4	30	45	60	90	120	30	45	60	90	120
Tensile strength (kg. per sq. cm.)	Whole rubber, 34.8(—)	51	73	15	—	—	49	50	15	—	—
	Group I 16.6(19.5)	—	—	—	— (it was so plastic that it could not be removed from the mold)		—	—	—	—	13
	Group II 20.5(22.9)	—	—	—	38	56	—	—	—	12	14
	Group III 23.5(24.9)	—	—	24	44	—	—	—	43	14	—
	Group IV — (—)	6	—	8	27	—	8	—	22	51	—
Modulus at 300% elongation (kg. per sq. cm.)	Whole rubber	8	14	6	—	—	4	18	10	—	—
	Group I	—	—	—	—	—	—	—	—	—	10
	Group II	—	—	—	6	16	—	—	—	8	8
	Group III	—	—	4	5	—	—	—	8	9	—
	Group IV	2	—	2	6	—	3	—	4	7	—
Elongation at break (%)	Whole rubber	952	835	395	—	—	825	725	338	—	—
	Group I	—	—	—	—	—	—	—	—	—	350
	Group II	—	—	—	852	742	—	—	—	320	320
	Group III	—	—	1000	940	—	—	—	775	345	—
	Group IV	560	560	818	—	—	1000	865	715	—	—
Combined sulfur (%)	Whole rubber	2.64	4.15	5.23	—	—	2.01	2.90	3.53	—	—
	Group I	—	—	—	—	3.83	—	—	—	—	3.34
	Group II	—	—	—	3.50	4.47	—	—	—	3.19	4.07
	Group III	—	—	3.66	4.58	—	—	—	3.22	4.32	—
	Group IV	0.85	—	1.97	4.39	—	2.15	—	4.17	4.87	—

In column (ii) the figures within parentheses indicate the molecular weights of unpurified rubber fractions.

TABLE 2

ACCELERATED PURE-GUM MIX

(Vulcanized at 134° C)

(i)	(ii)		(iii) Purified rubber						(iv) Unpurified rubber					
			Vulcanization (min.)						Vulcanization (min.)					
Property	Fraction and average molecular weight $\times 10^4$		10	20	30	45	60	90	10	20	30	45	60	90
Tensile strength (kg. per sq. cm.)	Whole rubber	34.8(—)	—	—	147	—	139	110	—	—	143	—	145	131
	Group I	16.6(19.5)	—	—	148	141	121	—	—	—	145	143	126	—
	Group II	20.5(22.9)	—	—	146	139	129	—	—	—	144	142	120	—
	Group III	23.5(24.9)	—	—	155	138	124	—	—	—	112	119	117	—
	Group IV	— (—)	140	149	144	—	—	—	146	173	166	—	—	—
Modulus at 500% elongation (kg. per sq. cm.)	Whole rubber		—	—	61	—	56	56	—	—	55	—	53	50
	Group I		—	—	20	21	17	—	—	—	25	27	23	—
	Group II		—	—	23	21	20	—	—	—	30	26	26	—
	Group III		—	—	32	29	27	—	—	—	32	32	31	—
	Group IV		20	24	27	—	—	—	23	32	34	—	—	—
Elongation at break (%)	Whole rubber		—	—	610	—	590	575	—	—	640	—	638	628
	Group I		—	—	860	832	808	—	—	—	758	765	755	—
	Group II		—	—	800	804	798	—	—	—	775	755	775	—
	Group III		—	—	735	715	710	—	—	—	710	710	715	—
	Group IV		842	782	760	—	—	—	775	750	742	—	—	—
Combined sulfur (%)	Whole rubber		—	—	2.52	—	2.66	2.69	—	—	2.35	—	2.53	2.59
	Group I		—	—	2.12	2.53	2.63	—	—	—	2.45	2.55	2.72	—
	Group II		—	—	2.37	2.74	2.94	—	—	—	2.61	2.68	2.78	—
	Group III		—	—	2.57	2.78	2.95	—	—	—	2.57	2.61	2.70	—
	Group IV		1.39	2.09	2.43	—	—	—	1.69	2.32	2.64	—	—	—

In column (ii) the figures within parentheses indicate molecular weights of unpurified rubber fractions.

TABLE 3

TIRE-TREAD TYPE MIX

(Vulcanized at 134° C)

(i)	(ii)		(iii) Purified rubber						(iv) Unpurified rubber					
			Vulcanization (min.)						Vulcanization (min.)					
Property	Fraction and average molecular weight × 10^4		10	20	30	45	60	90	10	20	30	45	60	90
Tensile strength (kg. per sq. cm.)	Whole rubber	34.8(—)	—	—	252	—	220	150	—	—	230	—	172	169
	Group I	16.6(19.5)	—	—	185	233	227	—	—	—	200	238	222	—
	Group II	20.5(22.9)	—	—	216	236	209	—	—	—	226	218	212	—
	Group III	23.5(24.9)	—	—	187	202	167	—	—	—	219	201	183	—
	Group IV	— (—)	113	182	177	—	—	—	127	238	263	—	—	—
Modulus at 300% elongation (kg. per sq. cm.)	Whole rubber		—	—	121	—	171	—	—	—	104	—	149	162
	Group I		—	—	81	112	128	—	—	—	82	105	120	—
	Group II		—	—	99	127	148	—	—	—	90	118	131	—
	Group III		—	—	116	148	163	—	—	—	100	133	150	—
	Group IV		73	118	153	—	—	—	39	86	117	—	—	—
Elongation at break (%)	Whole rubber		—	—	490	—	356	254	—	—	520	—	355	330
	Group I		—	—	495	495	450	—	—	—	505	500	438	—
	Group II		—	—	506	470	402	—	—	—	550	480	455	—
	Group III		—	—	430	385	325	—	—	—	480	395	335	—
	Group IV		472	434	368	—	—	—	550	538	500	—	—	—
Combined sulfur (%)	Whole rubber		—	—	2.01	—	2.17	2.48	—	—	2.03	—	2.55	2.73
	Group I		—	—	1.55	1.94	2.13	—	—	—	1.89	2.42	2.51	—
	Group II		—	—	1.42	1.92	2.38	—	—	—	1.55	2.11	2.41	—
	Group III		—	—	1.53	2.02	2.31	—	—	—	1.72	2.32	2.52	—
	Group IV		0.84	1.19	1.66	—	—	—	0.87	1.62	2.05	—	—	—

In column (ii) the figures within parentheses indicate the molecular weights of unpurified rubber fractions.

goes to the formation of effective cross-links. Bloomfield[6] has shown that, during vulcanization, rubber and sulfur can combine to form polysulfides of the formula $R-S_x-R$, where R is the rubber molecule, and x can be 1–4. Bloomfield has also suggested the possibility of sulfur entering cyclic rings formed by intramolecular cyclization of the rubber molecule during vulcanization.

Except in Group IV, purified rubber shows a higher combined sulfur than unpurified rubber in the rubber-sulfur mix in all the cures studied. In the tire-tread mix, on the other hand, the fractions of unpurified rubber show a higher combined sulfur than the corresponding fractions of purified rubber. In the accelerated pure-gum mix, the purified rubber gives sometimes higher and sometimes lower combined sulfur than the unpurified rubber.

All the fractions of purified rubber show a higher modulus than the corresponding fractions of unpurified rubber in the tire-tread type of mix.

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THE HYSTERESIS OF VULCANIZED RUBBER *

JACQUES CLOUAIRE

FRENCH RUBBER INSTITUTE, 42 RUE SCHEFFER, PARIS, FRANCE

INTRODUCTION

The present paper is based on an extensive investigation of the tensile properties of vulcanized natural rubber, carried out at the French Rubber Institute from April 1944 to December 1946. The purpose of this paper is to show how, in problems such as hysteresis, the correlation of certain experimental facts which apparently bear no relation to one another may lead to an explanation of the phenomenon involved.

The hysteresis effect shown by both natural rubber and synthetic rubbers after stretching has been recognized for a long time, and it can be defined as the nonsuperposition of the strain and recovery curves of one complete cycle of deformation. It should be noted that this definition makes no reference to the causes of the phenomenon nor to the idea of loss of energy, which is not so clearly defined as generally believed.

As a matter of fact, although the literature on the elasticity of rubber is remarkably extensive[1], little information is to be found on the underlying causes of hysteresis. The only real experimental work on the subject was carried out by Bouasse[2], who succeeded in throwing light on some of the complexities of the phenomenon. However, it appears that since that time little attention has been paid to his work. This may account for the fact that the idea of hysteresis being due solely to internal friction is still so widely accepted, although actually so completely incorrect.

THE CHIEF EXPERIMENTAL CHARACTERISTICS OF HYSTERESIS

The investigation was confined to a single mixture, representing the practical type of natural rubber vulcanizate known as "pure gum". Its actual composition was as follows:

Smoked sheet rubber	100
Sulfur	2.5
Butyraldehydeaniline	0.8
Stearic acid	0.25
Aldol-α-naphthylamine	0.5
Zinc oxide (active)	2

This mixture was vulcanized 15 minutes at 143° C, and was then placed in a Geer oven at 70° C for eight days to bring about post-vulcanization, which improved the elastic properties, increased the vulcanization plateau, and decreased the rate of subsequent aging. The product had a tensile strength of 200 kg. per sq. cm. (based on the original cross-section) and elongation at rupture of 800 per cent.

The type of test-specimen used was the standard Schopper ring and the tensile machine the L'Homme and Argy dynamometer (test-specimen and

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equipment), the advantages of which for the kind of testing in the present investigation have already been described[1]. The dynamometer was equipped with a device for automatically reversing the motion of the test-specimen and making it possible to describe deformation cycles between any two predetermined elongations with a cycle counter.

In following this procedure, five general precautions should be observed:

(1) The test-specimens should be uniform, so that valid comparative results are obtained; the specimens should be cut out with a sharp lubricated knife from a perfectly homogeneous vulcanizate which has been prepared under carefully controlled conditions, contains the proper antioxidizing agent for protection, and has been stored in darkness at about 20° C.

(2) The temperature during testing should be maintained at 20° ± 1° C.

(3) The humidity of the air should be 50–70 per cent.

(4) Three test-specimens should be sufficient to obtain reliable results when the breaking strength and ultimate elongation are not concerned.

(5) The rate of traction should be 30 cm. per minute. It was found that there is no appreciable difference in the results obtained within the range of 1 mm. per minute and 1 meter per minute.

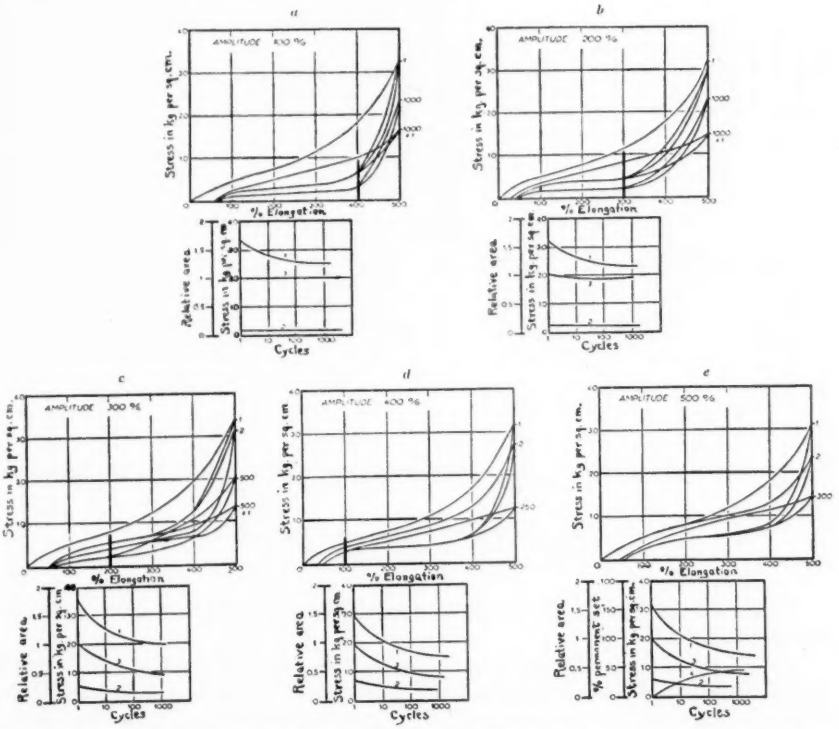

FIG. 1.—Tensile hysteresis tests for a maximum elongation of 500 per cent and cycle amplitude from 100 to 500 per cent (a, b, c, d, and e).

Curve 1—Change in maximum.
Curve 2—Difference in stress (mean elongation).
Curve 3—Relative change in area.
Curve 4—Permanent set.

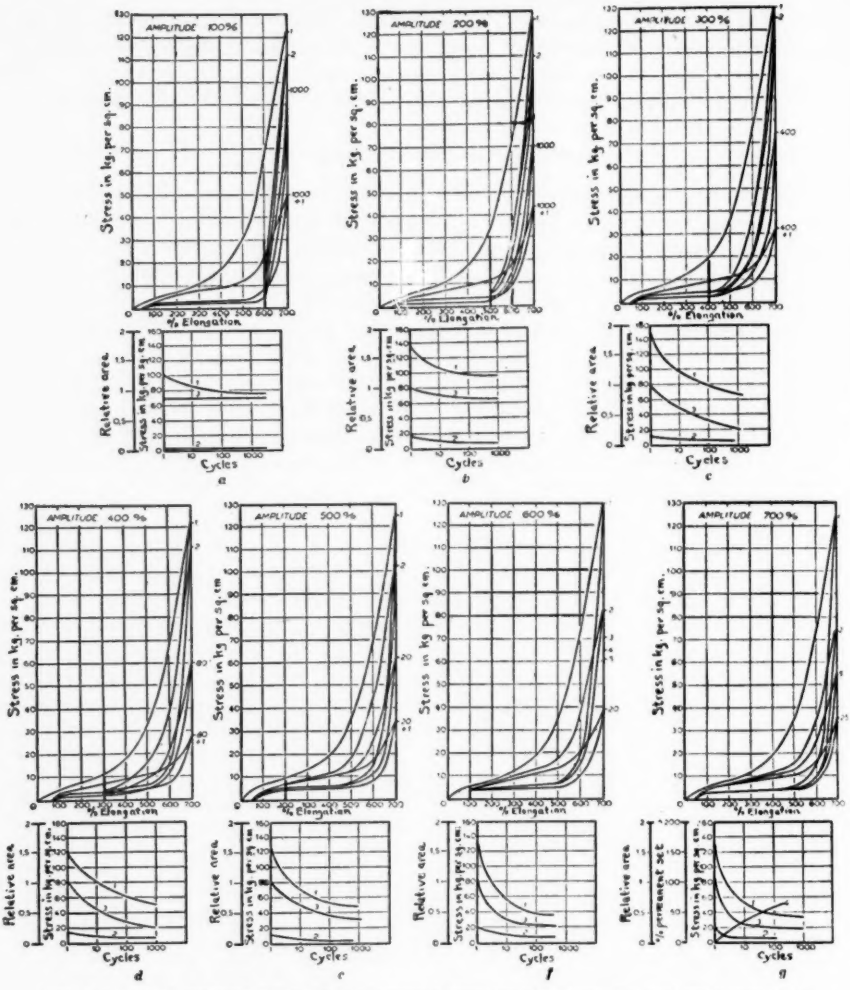

FIG. 2.—Tensile hysteresis tests for a maximum elongation of 500 per cent and cycle amplitude from 100 to 700 per cent (a, b, c, d, e, f, and g).

Curve 1—Change in maximum.
Curve 2—Difference in stress (mean elongation).
Curve 3—Relative change in area.
Curve 4—Permanent set.

Some of the most characteristic experimental results are summarized in Figures 1, 2, and 3.

In place of the ordinary type of hysteresis test, where the elongation is varied from zero to a predetermined maximum value, the hysteresis loops shown in Figures 1, 2, and 3 represent cyclic deformations between two limiting elongations, the lower limit being a series of values intermediate between zero and the maximum elongation, the highest to which the test-specimen was subjected.

In this way it was possible to demonstrate, as shown by the data in Figures 1 and 2, the influence of the amplitude of increasing cycles, *viz.*, 100, 200, and

300 per cent (calculated on a basis of the initial length) for a maximum constant elongation of 500 per cent (Figure 1) and 700 per cent (Figure 2).

On the other hand, Figure 3 shows, for an amplitude with constant cycle of 200 per cent, the influence of increasing the maximum elongation successively from 300 to 400 to 500 to 600 to 700 per cent.

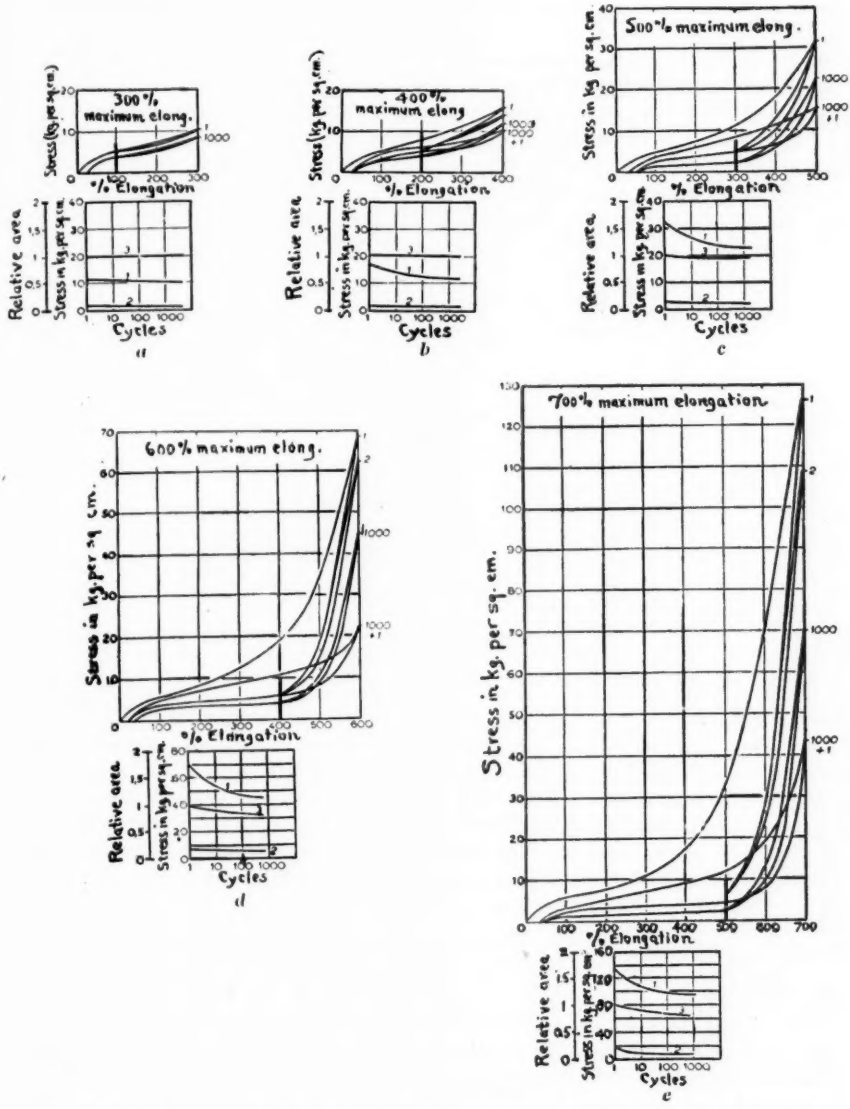

FIG. 3.—Tensile hysteresis tests for a constant amplitude of cycle of 200 per cent and maximum elongations from 300 to 700 per cent (a, b, c, d, and e).

Curve 1—Change in maximum.
Curve 2—Difference in stress (mean elongation).
Curve 3—Relative change in area.

Actually the tests were still more comprehensive than this, and included the whole range of maximum elongations and amplitudes between zero and 700 per cent. However, for the sake of clarity, not all the cycles are represented on the graphs, but only certain ones, the order numbers of which are shown on the right vertical scale of the diagrams.

The stress-strain curves shown on each of these diagrams, which were chosen as quite representative, are easy to interpret and show in succession: (1) an initial elongation to the maximum elongation selected; (2) an initial cycle between the two limiting elongations to which the test-specimens were stretched; (3) an *n*th cycle between these two limiting elongations; (4) complete retraction; and (5) a final cycle between rest and the maximum elongation.

From the hysteresis loops obtained in this way by automatic recording of the stress as a function of the elongation, several parameters were derived, the variations of which as a function of the number of cycles give a clearer idea of the whole phenomenon. These variables are represented by the curves numbered 1, 2, 3, and 4 below the stress-strain curves in Figures 1, 2, and 3.

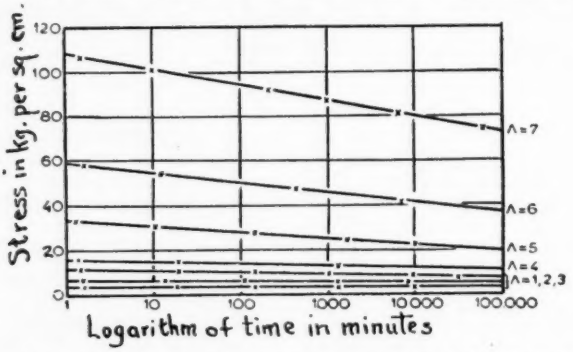

FIG. 4.—Relaxation of tension τ_0 in kg. per sq. cm. for a series of static elongations as a function of the logarithm of the time in minutes.

The curves numbered 1 show, as a function of the number of cycles, the ascent to the peak, *i.e.*, the progressive decrease in stress each time that the elongation reaches its maximum value; the curves numbered 2 show the differences in stress during traction and recovery for the intermediate elongation; the designated curves 3 show the relative changes in area of the hysteresis cycles, except that the immediate set, *i.e.*, the residual elongation at rest, is represented on the curves numbered 4 when the stress has become zero for each cycle (curve e in Figure 1 and curve g throughout (see Figures 1 and 2)), several general facts are manifest.

(a) The smaller the amplitude, the less the shift of the cycles.

(b) The smaller the amplitude, the smaller is the relative hysteresis loss as indicated by the area of the cycle with respect to the total area between the stress curve, the abscissa axis and the two limiting vertical axes; in other words, the ratio of the energy not returned to the machine to the energy which the machine has furnished in mechanical form during elongation of the test-specimen.

(c) As a consequence of fact (a), the greater the amplitude, the smaller is the limiting stress, as determined by extrapolation.

(d) The extreme limits of these tests, where the amplitude is the influential variable, are represented by relaxation tests, in which the variations in stress

at constant elongation (see Figure 4) and ordinary hysteresis tests, in which cycles in the range of zero and a predetermined maximum elongation[3]. It is of interest also to compare Figure 4 which shows the stress at constant elongation as a function of the logarithm of time (expressed in minutes) with the curves numbered 1 in Figures 1, 2, and 3, which represent the shift in the peak as a function of the logarithm of the number of cycles for different amplitudes. Actually in the data in Figure 4 the amplitudes can be considered to be zero.

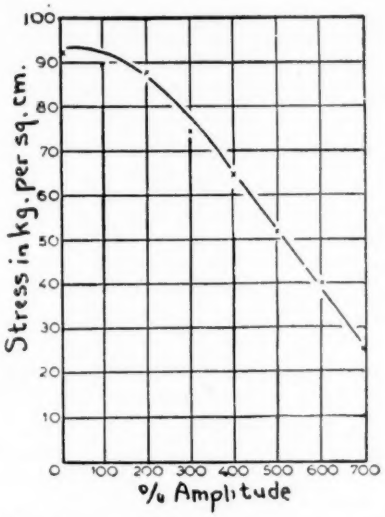

FIG. 5.—Limiting value of the tension τ_0 calculated by extrapolation to an infinite number of cycles for an elongation of 700 per cent as a function of the cycle amplitude.

The change in the limiting stress corresponding to an infinite number of cycles as a function of the amplitude gives the curve represented in Figure 5 for a constant elongation of 700 per cent.

THE SUPPOSED CAUSES OF TRACTION HYSTERESIS

In considering the causes of hysteresis, the influence of the residual set may be disregarded provisionally, for although this set results in nonsuperposition of the curves, it does not cause any considerable hysteresis loss.

At small amplitudes, *e.g.*, 100 to 200 per cent, the hysteresis loss is small, and it does not seem unreasonable to attribute it to internal friction for the most part. This internal friction can, at small deformations, be rightfully considered to be a liquid friction, *i.e.*, where the opposing force is proportional to the rate of deformation. This hypothesis is of great aid in calculating the effects of absorbers, and makes possible the use of a well known differential equation of the second order.

For elongations between zero and 200 per cent, the residual set is absolutely negligible, and the successive cycles are superposed.

For higher elongations, *e.g.*, between 600 and 700 per cent, *i.e.*, for an amplitude of 100 per cent, the cycles are in all cases very narrow, but they shift slightly parallel to one another (see Figure 2, curve a). This is explained by the fact that the relaxation is notable at high elongations, and in percentage is

practically the same within the range of 600 to 700 per cent. Neither the internal friction nor the residual set can account for the considerable hysteresis which is manifest above 200 per cent elongation and with amplitudes greater than 200 per cent.

It should be recalled at this point that, when vulcanized, pure natural rubber partially crystallizes when elongated beyond about 200 per cent, as has been demonstrated by numerous x-ray investigations[4]. Furthermore a recent study by Clark, Kabler, Blaker, and Ball has definitely proved by means of x-ray diagrams in experiments on relaxation phenomena[5], that this crystallization is by no means instantaneous. The experimental work of these authors led to the important conclusion that crystallization progresses with time and that there is an accompanying progressive decrease in stress.

THERMODYNAMIC NATURE OF CRYSTALLIZATION

In the problem under consideration, it is out of the question to consider crystallization as a reversible change in state, for in that case its magnitude would be absolutely defined as a function of two variables, elongation and temperature, with time having no influence.

It must not be forgotten that whereas crude rubber is ordinarily amorphous after it has been milled out into sheets, prolonged storage at ordinary temperatures changes it into the state of a "gel", which is actually a state of partial crystallization. This crystallization should be considered as an effect resulting from a spontaneous tendency toward a more stable state; but although the amorphous state is labile, it is nevertheless very resistant to change, and therefore the change to a more stable form is very slow. Deformation facilitates this change, but there is no definite and single state of crystallization corresponding to a definite state of deformation.

Crystallization progresses slowly, apparently toward an ultimate limit, but this is difficult to determine. This characteristic tendency toward spontaneous change indicates that crystallization is associated with a decrease in internal energy of the rubber.

It is easy to show[6] that the stress (based on the initial cross-section of the test-specimen) conforms to the following relation:

$$\tau = \left(\frac{\delta U}{\delta \lambda}\right)_T - T\left(\frac{\delta S}{\delta \lambda}\right)_T$$

where λ is the percentage elongation, T is the absolute temperature prevailing during the test, U is the internal energy, and S is the entropy. This equation is valid when the deformation is isothermic. The factor $T\left(\frac{\delta S}{\delta \lambda}\right)_T$ is negative, and represents the stress due to the kinetic nature of the elasticity of macromolecular substances[7]. For purely kinetic elasticity: $\frac{\delta U}{\delta \lambda} = 0$.

If this term is negative, as is the case of crystallization, the stress is smaller than the theoretical value for the amorphous phase. This confirms the conclusion, based on experiments of Clark, Kabler, Blaker, and Ball[5].

Under these conditions, the very nature itself of crystallization is a cause of the hysteresis phenomenon; in fact, for a given elongation crystallization is greater during recovery than during traction; hence the stress is less during recovery and, as a result, there is a hysteresis loop.

Experience has proved that when rubber is stretched it becomes considerably warmer, *e.g.*, in the present work, measurements with a thermoelectric couple showed temperature rises of 6 to 7° C, during ordinary elongation to 600 per cent[1] (see Figure 6).

According to the kinetic theory of elasticity of rubberlike materials, changes in entropy are chiefly responsible for this phenomenon. However, elasticity can still be explained by changes in internal energy, and the fact that the rapid rise in temperature, which is evident, for example, in Figure 6, coincides with the appearance of crystallization would seem to indicate that these changes play an important part in the heating effect during traction.

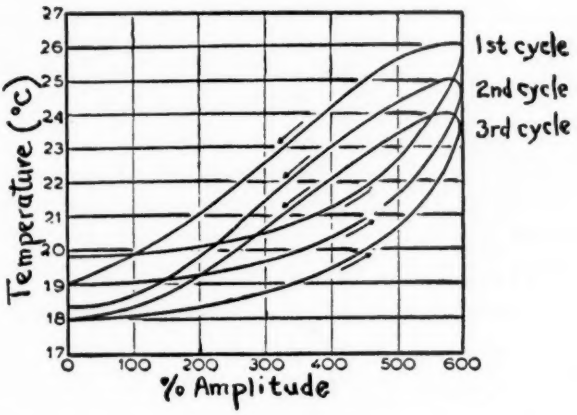

FIG. 6.—Change in temperature of a Schopper ring as a function of the elongation during successive tension cycles.

It follows from these considerations that even if there is no absolutely rigorous proof that retarded crystallization is the preponderant cause of hysteresis, it is nonetheless highly plausible. Only by quantitative measurements would it be possible to obtain positive proof, for only by such measurements could the extent of crystallization at a given elongation and the resultant change in internal energy be determined. However, measurements of this kind have not yet been made with absolute precision. Furthermore, a quantitative study of the degree of instantaneous crystallization would encounter technical difficulties because of the impossibility of obtaining x-ray diagrams with a sufficiently short time of exposure (0.1 second would be necessary)[8].

In conclusion, it should be added that a comparison with synthetic rubbers lends support to these ideas. It is well known, in fact, that only Neoprene crystallizes well[9] and at the same time shows a hysteresis phenomenon comparable to that of natural rubber, even though less intense. Synthetic copolymers do not crystallize, and when they are not loaded with carbon black they show hysteresis effects which depend chiefly on their permanent deformation, which is relatively great.

An interesting case is that of GR-S loaded with carbon black[10]. This copolymer shows a hysteresis loss which is greater after small elongations than after higher elongations. Since it does not crystallize, only plastic flow and internal friction would seem to be the causes of such hysteresis, at least in the light of present knowledge. These two phenomena are very important in the

case of GR-S; for plastic flow is an inherent property of GR-S, which is considerably more plastic than natural rubber with no crystallization to modify the plastic flow, while the internal friction results from high loadings of carbon blacks.

All discussion of the theoretical aspects of hysteresis, of the underlying causes of the phenomenon, and any mathematical interpretation have been purposely avoided in the present paper. However, it has been shown that, by purely experimental methods, the interesting conclusion may be drawn that the hysteresis phenomenon and also crystallization are interrelated phenomena, and that in no other elastomer are these phenomena more marked than in natural rubber.

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HYSTERESIS AND HEATING IN VULCANIZED RUBBER *

S. OBERTO AND G. PALANDRI

PIRELLI S.P.A., MILAN, ITALY

The use of synthetic rubbers, all of which have proved to possess elastic properties inferior to those of natural rubbers, and consequently transform a greater percentage of deformation energy into heat, has led to the necessity of improving methods for testing hysteresis. Dillon and Gehman[1] have already published a very detailed description and discussion of the various methods employed for measuring the hysteresis in rubberlike materials. We shall in this report confine ourselves to describing only two new test methods developed in the Pirelli Research Laboratories in 1943, to giving some of the results obtained, and to making some comments on the research work done during the last few years.

The general problem of the measurement of heating generated by hysteresis losses in cured rubber submitted to periodical stresses can be summarized as follows:

(a) Determination of the stress or strain values of cured rubber products.
(b) Evaluation from laboratory tests of the energy converted into heat per cycle and per unit of volume as a function of stress or strain amplitude and temperature.
(c) Determination by theoretical or graphical calculations, or by means of models, of the distribution of temperature, due consideration being taken of the cooling conditions of the surfaces of the specimen.

The nonuniform distribution of temperature, as per (c), influences the generation of heat by hysteresis locally, but this is not very important, as the relation hysteresis-temperature can be determined by laboratory tests.

The rigidity modulus also varies with the temperature, and the stress values therefore depend on the temperature distribution, as in (c). It is, however, possible in simple cases to solve the general problem by means of approximate methods.

It must be assumed that the form of the stress cycles in service conditions is the same as that applied on the specimens used for the laboratory tests, or that, within certain limits, the form of the cycle only slightly affects the energy losses when operating at the same deformation or stress conditions and at the same frequency. Laboratory tests should in any case be carried out with almost sinusoidal cycles.

Laboratory tests should determine the amount of energy converted into heat per cycle and per cubic centimeter of cured rubber as a function of the stress or strain amplitude and temperature.

We shall in our considerations refer to shear deformations, which are more easily obtained without causing stress alterations at the points where the

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sample is fixed. This is also the type of strain most common in normal applications.

The oscillation as a result of the shear stress is perfectly symmetrical on each side of the nil-deformation position, and therefore elongation and creep phenomena, which are always present in a uni-directional deformation due to compression or elongation, need not be considered.

In this paper we shall also give a brief description of some experimental results obtained with a method recently developed for testing rubber specimens by means of periodical tension stresses superimposed to a permanent static elongation. With this method it is possible to provoke symmetric oscillations on each side of the static deformation position, and we think it can be usefully applied for some particular applications.

Let ρ be the shear strain in radians which varies periodically with the frequency f. The quantity of energy converted into heat per unit of volume is:

$$W = K(t)\rho^2 f \tag{1}$$

The quadratic dependence of deformation is generally accepted, and it will be seen that this is met within certain limits. The coefficient K, which varies with the temperature, is therefore the energy dissipated in Joule units at a given temperature in a single cycle per cubic centimeter of cured stock with a shear amplitude of one radian. The value of ρ, adopted to calculate the deformation, should not be great enough to become destructive (due to the heat developed and the sharp temperature rise), nor small enough to be negligible for the evaluation of the heat due to hysteresis.

The following relation between shear stress (kg. per sq. cm.) and deformation (radians) is also of fundamental importance:

$$\tau = G(t)\rho \tag{2}$$

τ being the specific shear stress (kg. per sq. cm.) and G the dynamic shear modulus, which is strictly dependent on the temperature. The linear relation, especially for high loaded stocks, is valid only for a first approximation. In this case the value of G is different for $\rho = 0.05$ and $\rho = 0.2$ radians. The different values for G obtained by various experimenters, or by following different methods, can be explained by the different stresses used for the test. In our calculations the value of G will of course be determined by the same deformation as used for the determination of K.

In accordance with the above we shall determine the relations of $K(t)$ and $G(t)$ with the hysteresis measuring set in the laboratory. Knowing these relations, it is also possible to calculate the energy loss per cycle under constant force instead of constant amplitude. In fact from Equations (1) and (2) we have:

$$\rho = \frac{\tau}{G} \qquad \text{and} \qquad W = \frac{K}{G^2}\tau^2 f$$

and calling:

$$\frac{K}{G^2} = L \tag{3}$$

we have:

$$W = L(t)\tau^2 f$$

where L is a new coefficient, also dependent on the temperature. L at a given temperature is the energy loss in Joule units per cubic centimeter for a sinusoidal shear deformation cycle having a maximum load of 1 kg. per sq. cm.

Knowing K, G and the calculated value L, it is possible in many simple cases to evaluate the hysteresis losses as a function of the applied force or deformation. These data are not sufficient in themselves, however, to evaluate the temperature distribution due to heat generated by hysteresis, and consideration should also be given to the thermal conductivity and to the rate of heat dissipation in the surroundings due to radiation and convection. The effect of the thermal conductivity on the temperature rise has not been quantitatively considered in the different flexometer tests (Goodrich and others).

The thermal conductivity is practically the same for common rubberlike polymers and for light loaded stocks, but increases very rapidly in high black loaded stocks. Certain qualities of black confer very high conductivity, and this must be taken into account when estimating the heating generated by hysteresis and in evaluating results.

Let us now consider a system in which the outside surfaces maintain a constant temperature not influenced by the heat generated within the system. If the heat generated and the thermal conductivity in the sample both double their values when working in temperature equilibrium, then the distribution of temperature remains the same. In fact the fluxes are linearly dependent on the temperature and conductivity.

When in temperature equilibrium, it is better to consider the ratio $\frac{K}{\lambda}$ instead of K as the heating factor, as this is in fact an energy loss factor, λ being the thermal conductivity coefficient. For the same reason we shall consider the ratio $\frac{L}{\lambda}$ instead of the value L. To have homogeneous units as the numerator and denominator of the ratio, being λ measured in thermal units, we shall express K and L also in calories instead of dissipated Joule units. These two symbols thus take the index q and become Kq and Lq, respectively.

In uniformly stressed rubber plates and cylinders, in which the surfaces are maintained at constant temperature, the maximum temperature reached will be fairly proportional to the mean value $\frac{Kq}{\lambda}$. The proportionality would be perfect if Kq and Lq were independent of the temperature. In temperature equilibrium condition we have, therefore, a better approximate evaluation of heating in rubber stocks due to hysteresis if the ratio $\frac{Kq}{\lambda}$ is considered instead of the simple value K.

TEST METHODS

Both the test methods now being used in our Laboratories employ forced oscillations at resonance. In the first method the rubber sample is submitted to periodical shear stresses in an electrically driven apparatus; in the second, the rubber sample, which is kept in permanent strain, undergoes periodical tension stresses, also in an electrically driven apparatus.

Under normal conditions the deformation amplitudes are generally small, but they become considerably larger when operating at critical resonance condition. Both these methods, which employ forced oscillations tuned to resonance to the rubber mass system, have proved to be very practical for the determination of hysteresis losses and dynamic elastic modulus.

Shear test method.—The test apparatus now being used in the Pirelli Research Laboratories is schematically shown in Figure 1, and a photograph is reproduced in Figure 2.

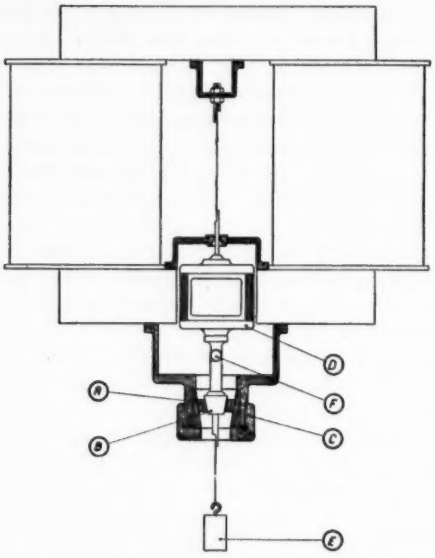

FIG. 1.—Schematic drawing of resonance shear apparatus.

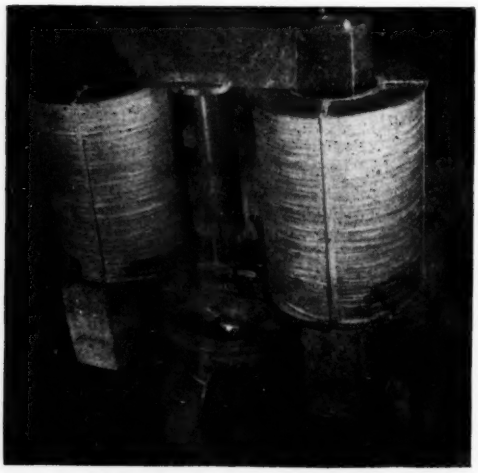

FIG. 2.—Resonance shear apparatus.

The rubber sample A has the form of a truncated cone ring and, by means of the rotor B, is subjected to shear stresses at the desired frequency. This rotor is fixed to the coil D driven electrically in a magnetic field by the current generated from a 50-watt amplifier-oscillator unit of the beat frequency type (range of frequency 0 to 10,000 cycles per second). The output impedance of the amplifier has been matched to the impedance of the moving coil, while the sinusoidal character of the current in the coil has been confirmed by means of a cathode ray oscillograph. The frequency of the oscillator can be varied

continuously from zero to that desired, a reed type frequency meter being used to measure the frequency up to 125 cycles per second. Higher frequencies are measured with a frequency bridge. It is possible to obtain resonance conditions at different frequencies with the same rubber samples by simply varying the value of the supplementary weights in the mass system.

The outer and inner surfaces of the rubber sample, which is ring-shaped as shown in Figure 3, are provided with triangular shaped teeth which correspond to similar ones on the rotor B and ring C, as shown in Figure 1. The sample is thus kept perfectly in position, this being facilitated by its conical shape and by the weight E applied to the rotor; this causes the rotor to adhere tightly to the supporting ring C and gives the sample a static compressive stress of $\sigma_c = 0.04$ kg. per sq. cm.

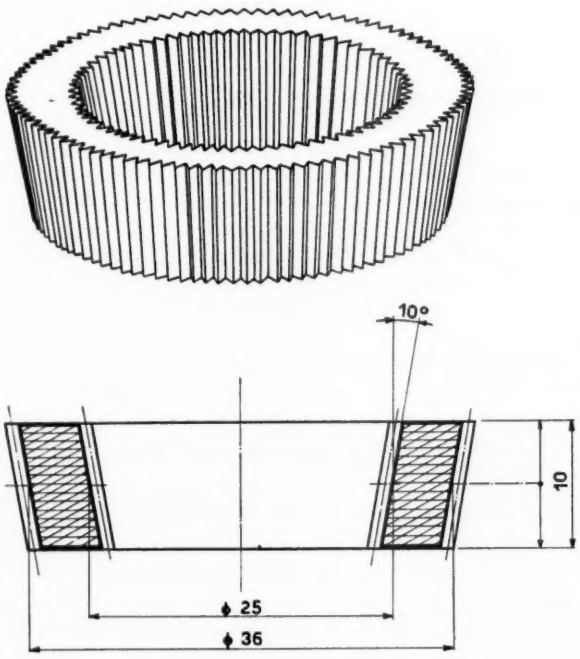

FIG. 3.—Test-specimen.

Deformation amplitudes are read on a transparent scale by means of a luminous line reflected by the concave mirror F on the coil D. The rubber samples can be heated during a test in a small air oven applied to the apparatus. The test temperatures are controlled by two electric thermocouples on the outer and inner surfaces of the test-specimen. The volume of the sample is 3.43 cubic centimeters, which is relatively small and allows reduced scale tests when only a limited quantity of stock is available.

It is possible also to measure the static shear modulus G by direct current or by a couple of weights applied to the system.

Determination of hysteresis losses and elastic modulus.—In an oscillating system such as that indicated above, the rubber sample acts as a torsional

spring with a spring stiffness $\frac{1}{C}$ (dyne cm. per radian) and a viscous resistance proportional to the rotating speed, b being the constant of proportionality (dyne-cm.-sec. per radian). If J is the moment of inertia of the oscillating system (g.-sq. cm.), α the rotation in radians, and $\Gamma \cos \omega t$ the impressed momentum[2] (dyne-cm.), where ω is the angular frequency and t the frequency, then we can write the motion equation as follows:

$$\Gamma \cos \omega t = J \frac{d^2\alpha}{dt^2} + b \frac{d\alpha}{dt} + \frac{\alpha}{C} \tag{1}$$

The solution of this equation, well known in alternating current problems in electricity, is:

$$\alpha = \frac{\Gamma \cos (\omega t - \theta)}{\sqrt{\left(\frac{1}{C} - J\omega^2\right)^2 + b^2\omega^2}} \text{ where } \tan \theta = \frac{b\omega}{\frac{1}{C} - J\omega^2} \tag{2}$$

Working in resonance amplitude conditions it is:

$$\omega^2 = \frac{1}{CJ} - \frac{b^2}{2J} \tag{3}$$

and Equation (2) becomes:

$$\alpha^{\max} = \frac{\Gamma \cos (\omega t - \theta)}{b\sqrt{\omega^2 + \frac{b^2}{4J^2}}} \text{ where } \tan \theta = \frac{2\omega J}{b} \tag{4}$$

When $\frac{b}{2J}$ is less than 1, as in our case, Equation (4) is reduced with small error to:

$$\alpha^{\max} = \frac{\Gamma \sin \omega t}{b\omega} \text{ where } \alpha^{\max} = A_{\max} \sin \omega t$$

Under these conditions Equation (3) becomes very nearly:

$$\frac{1}{C} = J\omega^2 \tag{5}$$

The energy losses through heat, *i.e.*, the hysteresis losses H, can be calculated as follows:

$$H = f \int_0^{2\pi} b \frac{d\alpha}{dt} d\alpha \text{ erg per second}$$

and solving:

$$H = \frac{\Gamma \omega A_{\max}}{2} 10^7 \text{ watt}$$

where $A_{\max}$ is the maximum deflection of the coil in radians. Dividing H by the weights (grams) or by the volume (cubic cm.) of the rubber sample, we obtain the watt/g. or watt/cc. losses.

To calculate the elastic modulus it is necessary to know the driving momentum; this differs from the impressed momentum, which only compensates the energy losses due to hysteresis. Equation (5), valid in resonance conditions, provides a direct method for the determination of the driving momentum.

In fact by knowing J (moment of inertia of the coil-rotor system), and measuring ω, and by calculating the spring stiffness $\frac{1}{C}\left(\frac{\text{dyne-cm.}}{\text{radian}}\right)$ by means of Equation (5), and knowing the maximum amplitude of rotation A_{max} (radians), we can also calculate the maximum value of the driving couple applied to the sample $\frac{A_{max}}{C}$.

From the value of the driving momentum it is possible to calculate the mean tangential specific stress which, referred to the strain, gives the dynamic shear elastic modulus G. When calculating the specific stress, mean values are taken, which, considering the size of the sample, differ very little from the maximum or minimum values.

To check the accuracy of the determination, we have made tests on various samples of the same stock, the height and thickness, as well as the number and dimensions of the teeth, being different in each case. The results obtained, within the limits of accuracy of the test method, are practically the same in all cases, and demonstrate that with our test method the modulus G and the energy losses do not depend on the shape of the sample.

Figures 4 and 5 show, respectively, the energy loss (watt per g.) and dynamic shear stress *versus* dynamic strain for two Hevea stocks with different black loading, and with specimens of various shapes and dimensions of teeth, as indicated above. Other special experiments have been made to investigate the effects of the variation in physical parameters, and include the measurement of the dynamic properties with varying frequency, static compressive stress, dynamic strain and temperature.

The variation in hysteresis losses at constant dynamic strain and temperature increases proportionally with the frequency, as shown in Figures 6 and 7. The dynamic shear modulus G of Hevea[3] and GR-S gum and tread stocks is seen to be independent of frequency in the range of 20 to 100 cycles per second (see Figures 8 and 9). Values of the static modulus are also plotted in Figures 8 and 9, and they are generally lower than the dynamic modulus.

The hysteresis losses at constant frequency and temperature seem to follow the quadratic law *versus* dynamic shear strain, especially for low loaded stocks (see Figures 10 and 11). With tread stock, the hysteresis losses are found to be lower than would be the case with the quadratic law.

The dynamic modulus G for Hevea gum stock at constant temperature is independent of dynamic shear strain up to a dynamic deformation of 0.2 radian (see Figure 12). This is not exactly true for GR-S gum stocks and for tread stocks where an increase in dynamic strain produces a decrease in modulus, especially at low temperatures (see Figures 12 and 13). The variation in dynamic modulus due to application of a static compressive strain, which with other methods of the shear type is very great, is practically nonexistent with our method.

Figures 14, 15, 16 and 17 give the results of dynamic modulus and hysteresis loss measurements on different gum and tread stocks with various static compressive stresses from 0.02 to 0.08 kg. per sq. cm. The fact that, with our method, the modulus and energy losses are independent of the static compressive stress is an important advantage when comparing it with other shear methods, according to which it is necessary to use high static compressive stress normal to the applied dynamic shear stress to avoid slippage during test, or to cement the rubber specimens to the platens, which procedure does not

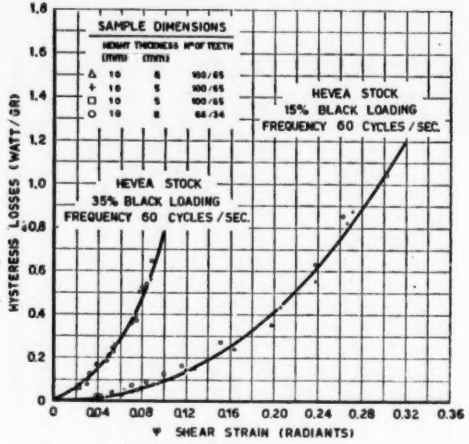

FIG. 4.

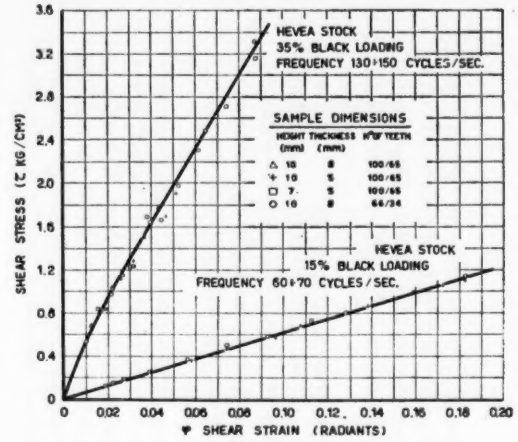

FIG. 5.

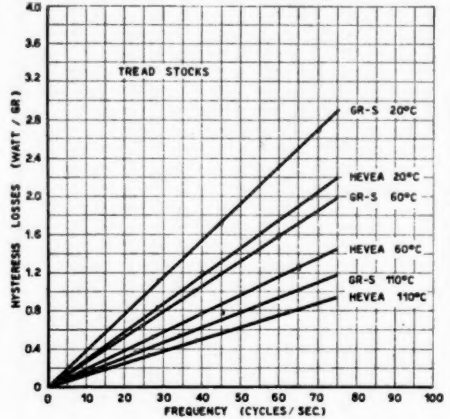

FIG. 6.

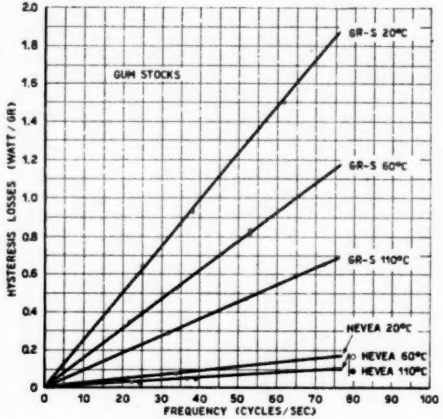

FIG. 7.

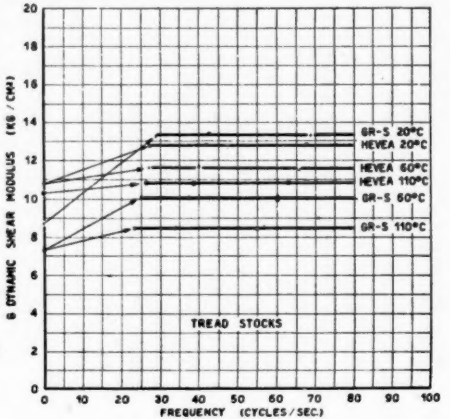

FIG. 8.

FIG. 4.—Hysteresis losses *vs.* shear strain with various sample shapes. FIG. 5.—Dynamic shear stress *vs.* shear strain with various sample shapes. FIG. 6.—Hysteresis losses *vs.* frequency of tread stocks. FIG. 7.—Hysteresis losses *vs.* frequency of gum stocks. FIG. 8.—Dynamic shear modulus *vs.* frequency [illegible]

FIG. 6.

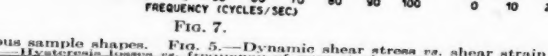

FIG. 7.

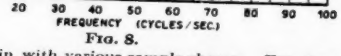

FIG. 8.

FIG. 4.—Hysteresis losses *vs.* shear strain with various sample shapes. FIG. 5.—Dynamic shear stress *vs.* shear strain with various sample shapes. FIG. 6.—Hysteresis losses *vs.* frequency of tread stocks. FIG. 7.—Hysteresis losses *vs.* frequency of gum stocks. FIG. 8.—Dynamic shear modulus *vs.* frequency of tread

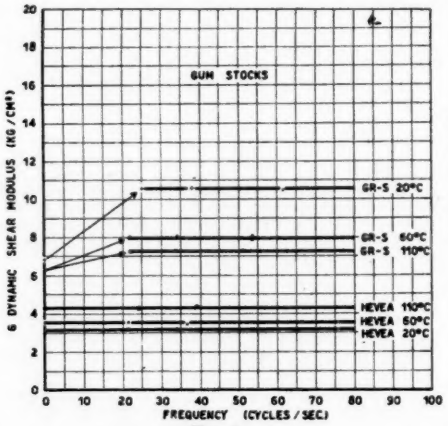

FIG. 9.

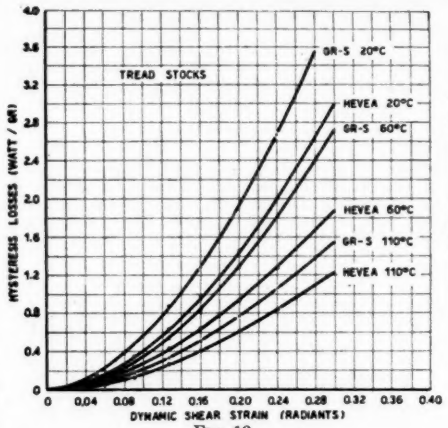

FIG. 10.

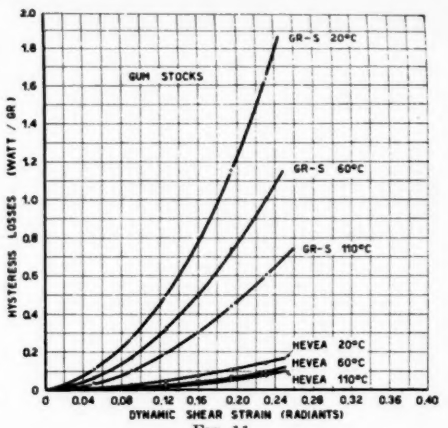

FIG. 11.

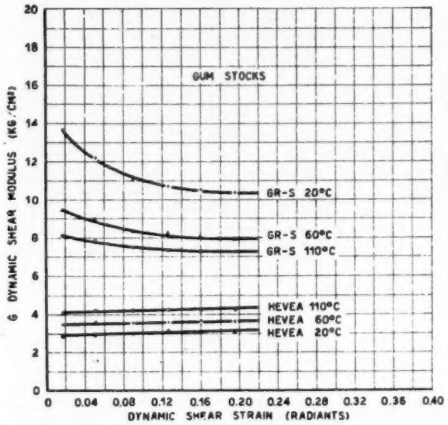

FIG. 12.

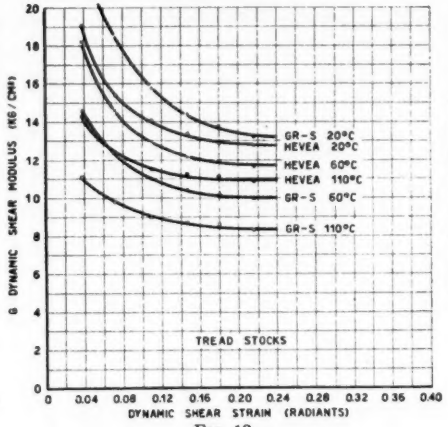

FIG. 13.

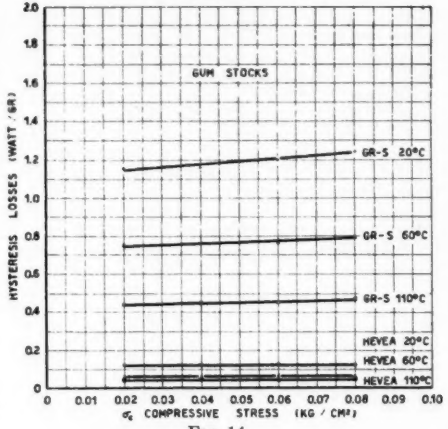

FIG. 14.

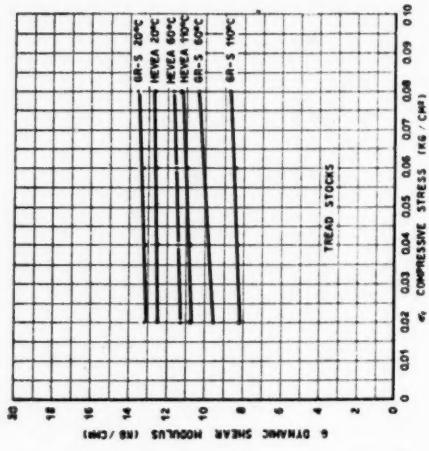

FIG. 17.

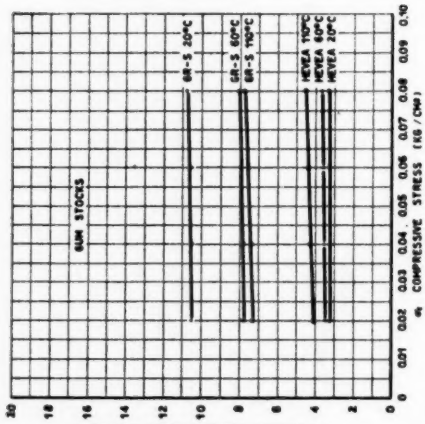

FIG. 16.

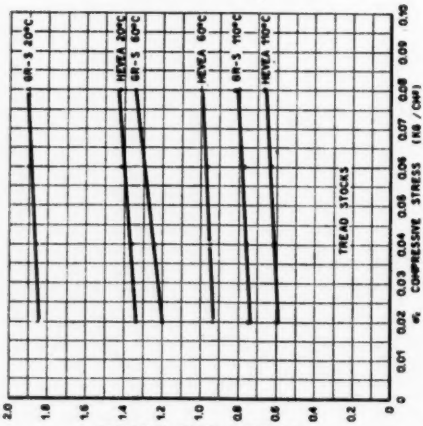

FIG. 15.

FIG. 9.—Dynamic shear modulus *vs.* frequency of gum stocks. FIG. 10.—Hysteresis losses *vs.* dynamic shear strain of tread stocks. FIG. 11.—Hysteresis losses *vs.* dynamic shear strain of gum stocks. FIG. 12.—Dynamic modulus *vs.* shear strain for gum stocks. FIG. 13.—Dynamic modulus *vs.* dynamic shear strain for tread stocks. FIG. 14.—Hysteresis losses *vs.* compressive stress of gum stocks. FIG. 15.—Hysteresis losses *vs.* compressive stress of tread stocks. FIG. 16.—Dynamic modulus *vs.* compressive stress of gum stocks. FIG. 17.—Dynamic modulus *vs.* compressive stress of tread stocks. (Note: Condition of test for Figures 9, 16, and 17—Dynamic shear strain, 0.2 radian; for Figures 10 and 11—Frequency, 50 cycles per sec.; for Figures 14 and 15—Dynamic shear strain, 0.2 radian, frequency, 50 cycles per sec.)

meet the requirements of practical tests. When applying high static compressive stress, the modulus depends a good deal on the compressive stress. With our conical ring-shaped specimen, in which the two stressed surfaces are continuous, the nonuniform static stress distribution occurring in samples where the two stressed surfaces are discontinuous is eliminated.

With our method, which is independent of static compressive stress[4], it is, therefore, possible to measure the real simple shear modulus.

The effect of temperature on dynamic modulus and energy losses can be seen from Figures 6 to 13. We have found that, in general, with increase in temperature the losses in modulus and energy are less.

Tension test method.—The apparatus now being used in the Pirelli Research Laboratories for the tension test is shown schematically in Figure 18, and in a photograph in Figure 19.

The four rubber samples A are of the ring type, as used in the Schopper dynamometer test, and are maintained in a permanent strain of the desired

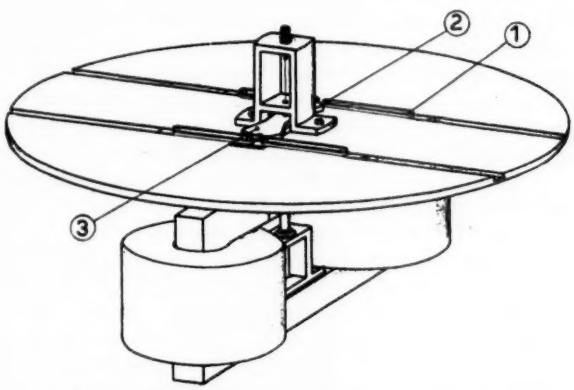

FIG. 18.—Drawing of resonance tension test apparatus.

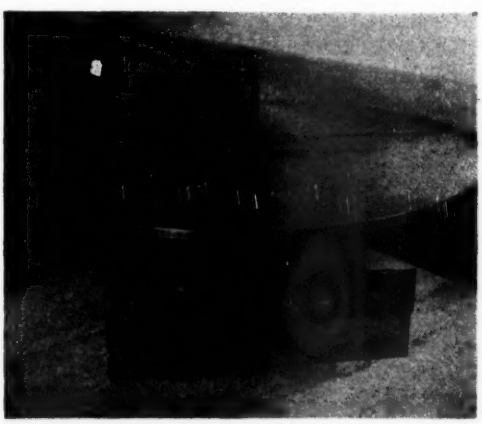

FIG. 19.—Resonance tension test apparatus.

value by means of the grooved pins indicated by 1 and 2 (see Figure 18). Pins 1 are movable and can be set at any position to elongate the specimens as desired, from 0 to 500 per cent. Pins 2 are set on the cross-arm 3, which is fixed to the coil driven electrically in a magnetic field by the current generated from an amplifier-oscillator unit of the beat frequency type, already described. Periodical tension stresses can in this way be superimposed with perfect symmetry on each side of the static deformation position of the specimen. Resonance conditions can be obtained at different frequencies, either by changing the size of the specimen or by using the same rubber sample and adding supplementary weights to the mass system. Deformation amplitudes are read on a transparent scale, as described in the shear test method.

It is possible also to measure the static elastic modulus E by means of direct current or by applying a couple of weights to the system. For the determination of hysteresis losses and elastic modulus, we follow the same method as described for the shear test method. The only difference is in the determination of the dynamic tension elastic modulus E, for which it is necessary to calculate the specific tension stress from the measured driving momentum, and the corresponding tension strain on the sample from the rotation of the cross-arm. To check the accuracy of the determination we have made tests with samples of different shapes and varying lengths and cross section.

The results reported in Figures 20 and 21, where different types of points are employed for different shaped samples, show that the dynamic modulus[5] E and the hysteresis losses are independent of the shape of the sample. Figures 22 and 23 give the hysteresis losses and dynamic tension modulus E at constant dynamic strain and temperature as a function of the static permanent deformation for Hevea and GR-S gum and tread stocks.

The hysteresis losses decrease rapidly with the static permanent strain to a minimum value corresponding to a static elongation of 110–130 per cent for gum stocks and 70–90 per cent for tread stocks. When this minimum has been reached, then the losses rise rapidly with increasing static permanent strain. The dynamic modulus E (Figure 23) behaves similarly, but the minima drop to lower values corresponding to a static deformation of 80–120 per cent for gum stocks and 20–50 per cent for tread stocks.

In Figures 24 and 25 we report the hysteresis losses, dynamic modulus *versus* frequency at constant dynamic tension strain, permanent static strain and temperature for GR-S gum and tread stocks. The hysteresis losses increase proportionally with frequency, while the dynamic modulus remains constant, as in the shear tests. Figures 26 and 27 show the relation of the hysteresis losses and dynamic modulus *versus* dynamic tension strain at constant frequency, static permanent strain, and temperature for Hevea and GR-S gum and tread stocks. The hysteresis losses seem to follow the quadratic law, while the dynamic modulus remains constant for Hevea gum stock but decreases very rapidly with increasing dynamic tension strain for Hevea tread and GR-S tread and gum stocks.

It is of interest to note that the ratio between E and G is about 3 for both gum and tread stocks when calculated from the dynamic tests. With this value the coefficient m in the Poisson equation becomes equal to 2, as found with other methods.

The ratio $\frac{G}{E}$ therefore becomes about $\frac{1}{3}$.

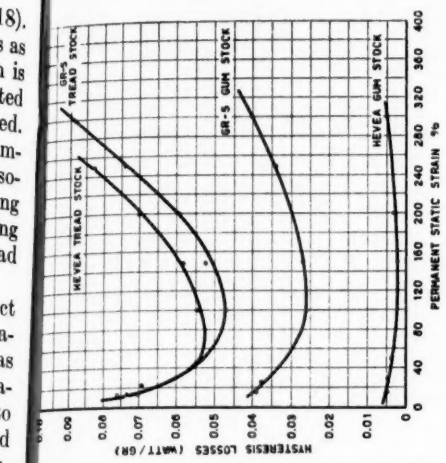

FIG. 22.

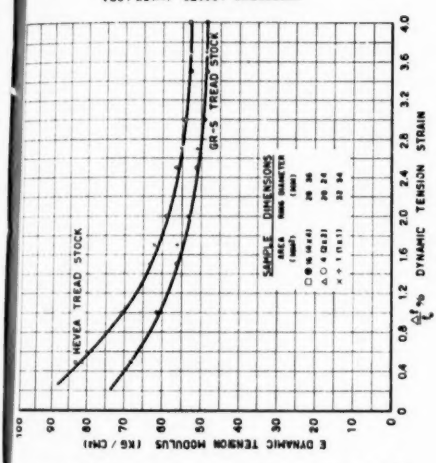

FIG. 21.

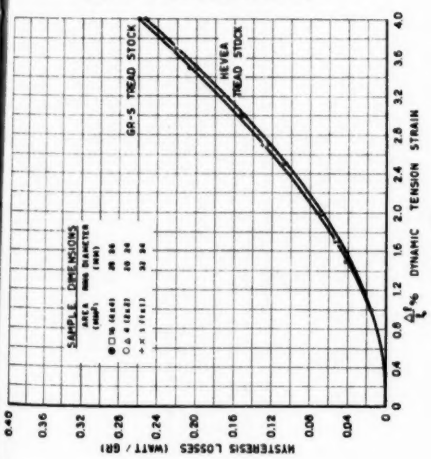

FIG. 20.

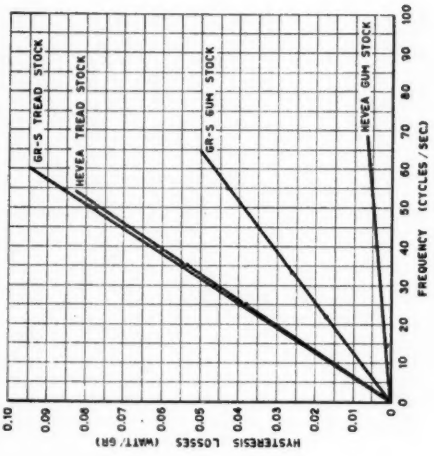

FIG. 24.

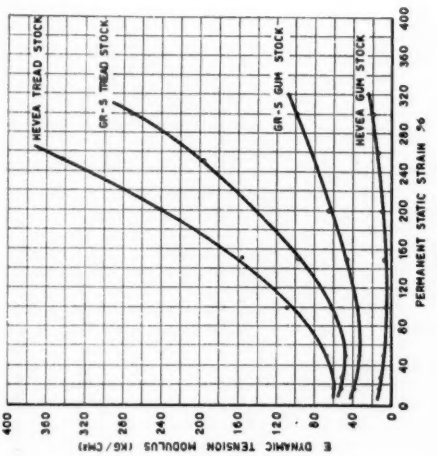

FIG. 23.

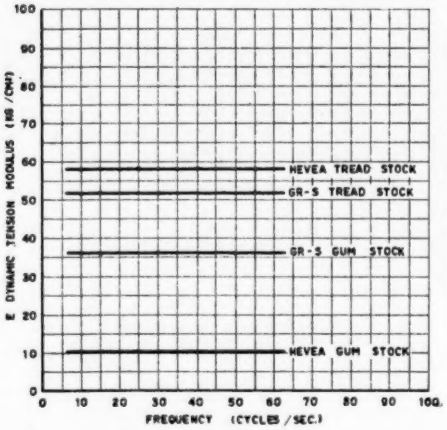

FIG. 25.

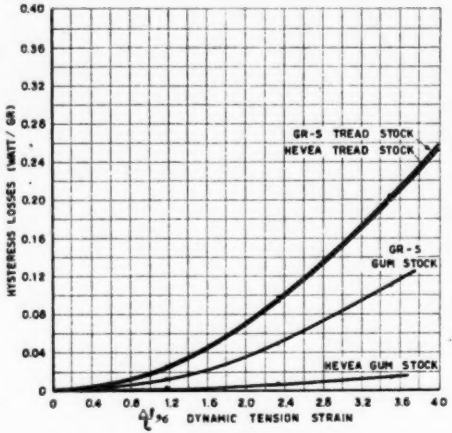

FIG. 26.

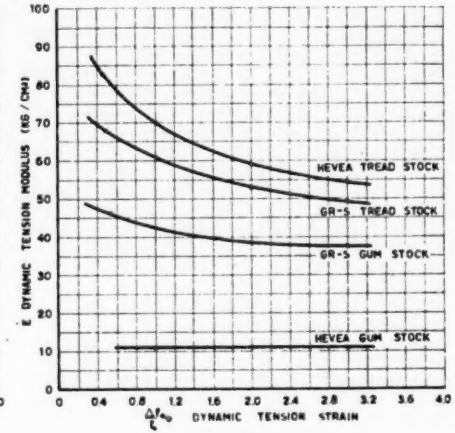

FIG. 27.

FIG. 20.—Hysteresis losses *vs.* tension strain with various sample shapes. FIG. 21.—Dynamic modulus *E vs.* tension strain with various sample shapes. FIG. 22.—Hysteresis losses *vs.* permanent static strain for tread and gum stocks. FIG. 23.—Dynamic modulus *E vs.* permanent static strain for tread and gum stocks. FIG. 24.—Hysteresis losses *vs.* frequency of gum and tread stocks. FIG. 25.—Dynamic modulus *E vs.* frequency of gum and tread stocks. FIG. 26.—Hysteresis losses *vs.* dynamic tension strain of gum and tread stocks. FIG. 27.—Dynamic modulus *E vs.* dynamic tension strain of gum and tread stocks. (Note: Conditions of test for Figures 20 and 21—Temperature of test, 20° C; permanent static strain, 15%; for Figures 22 and 23—Dynamic tension strain, 2%, frequency, 50 cycles per sec.; temperature of test, 20° C; for Figures 24 and 25—Dynamic tension strain, 2%, permanent static strain, 15%, temperature of test, 20° C; for Figures 26 and 27—Frequency, 50 cycles per sec., permanent static strain, 15%, temperature of test, 20° C.)

APPLICATION OF HYSTERESIS MEASUREMENTS

The effect of black loading on GR-S compounds.—The effect of black loading on GR-S compounds has been studied by preparing compounds containing different percentages of black of various qualities. The types chosen for the comparison are the following: EPC, SRF, FT, P.1250, which are few in number but representative of quite different qualities.

P.1250 black is of German production, its characteristics being between those of HMF and EPC blacks. It has considerable hardening properties, and confers a very high electric and thermal conductivity to the compounds.

The composition of the compound used for the test (parts by weight) is given in Table I below:

TABLE I

Standard GR-S	100.0
Mercaptobenzothiazole	0.7
Diphenylguanidine	0.8
Zinc oxide	5.0
Sulfur	1.0
Black	20/30/40/50

Acceleration is very high and the sulfur content correspondingly low, and this reduces the effect of the variable absorbing power *versus* accelerators of the different blacks used. It has been found possible to keep the cure time uniform at 60 minutes and 143° C for all compounds.

Figures 28 to 37 give the experimental values obtained at 30°–100° C, that is, at ambient temperature and at a temperature which should not be surpassed in service conditions for safety reasons. Figures 28, 29, 30 and 31 show, respectively, the values of G and K in mechanical units as a function of the black loading.

Besides the G and K values, the calculated value of L is given in Figures 32 and 33 as a function of the black loading. Figures 34 to 37 give the calculated values of the ratios $\frac{Kq}{\lambda}$ and $\frac{Lq}{\lambda}$ still *versus* black loading.

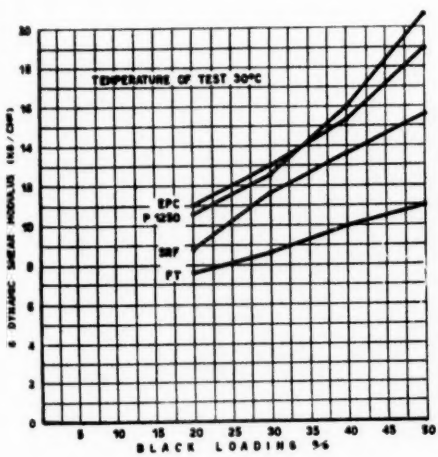

FIG. 28.

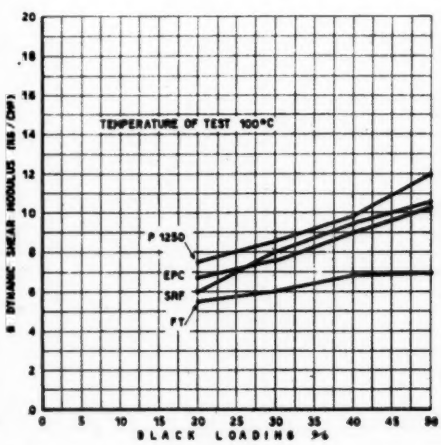

FIG. 29.

FIGS. 28 and 29.—Dynamic shear modulus *vs.* black loading of different GR-S stocks, at temperatures indicated.

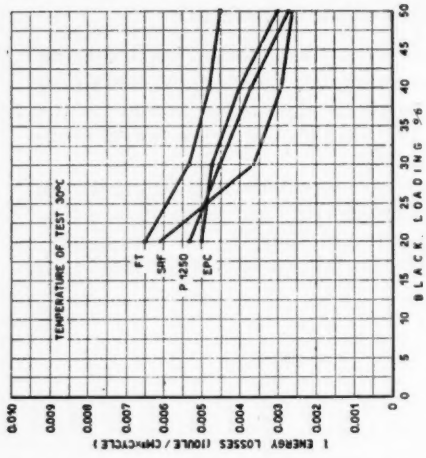

FIG. 32.

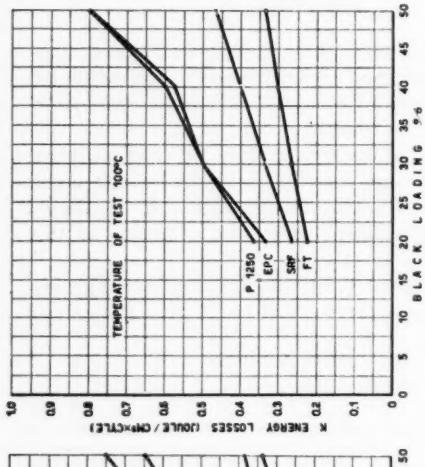

FIG. 31.

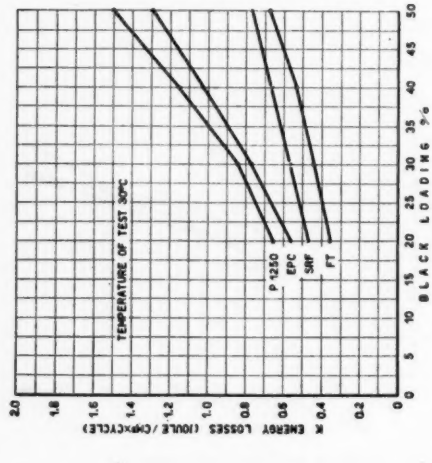

FIG. 30.

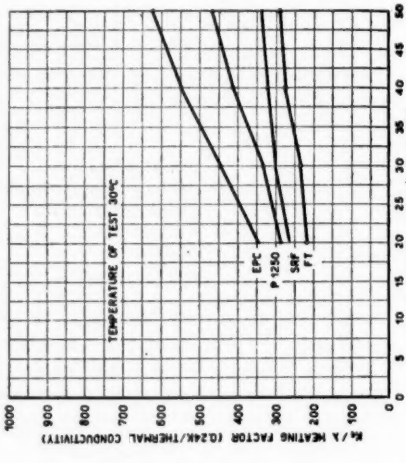

FIG. 34.

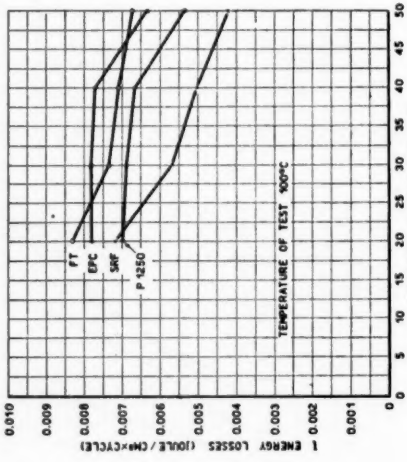

FIG. 33.

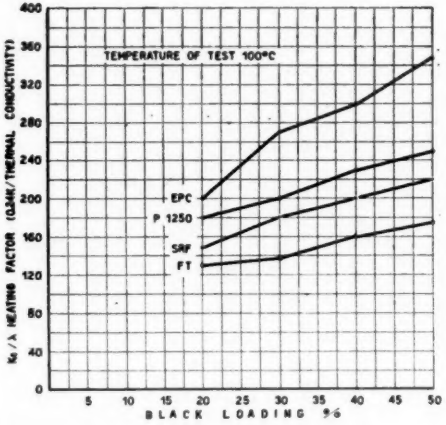

FIG. 35.

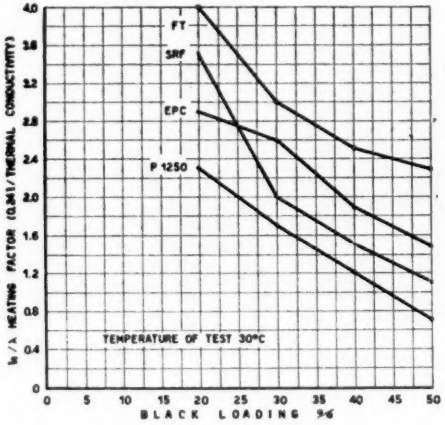

FIG. 36.

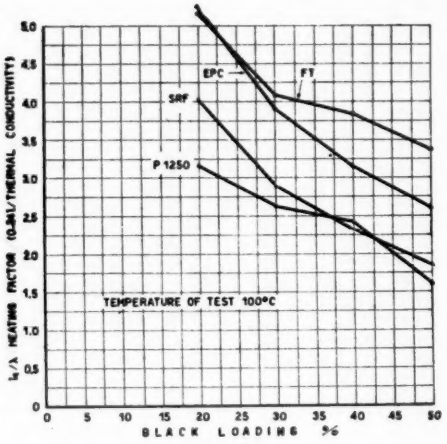

FIG. 37.

FIGS. 30 and 31.—Energy loss at constant strain K *vs.* black loading for different GR-S stocks. FIGS. 32 and 33.—Energy loss at constant force L *vs.* black loading for different GR-S stocks. FIGS. 34 and 35.—Heating factor at constant strain $\frac{Kq}{\lambda}$ *vs.* black loading for different GR-S stocks. FIGS. 36 and 37.—Heating factor at constant force $\frac{Lq}{\lambda}$ *vs.* black loading for different GR-S stocks. (Temperatures of tests are indicated on graphs.)

The coefficient λ was determined by direct measurement of the thermometric conductivity between 20° and 80° C and from the calculated specific heat. The same thermal conductivity value has been assumed for the two temperatures 30° and 100° C, owing to the difficulty of making very exact measurements within these limits and the relatively small importance of the correction.

An examination of the results reported in Figures 28 to 37 illustrate the following.

(a) Figures 28 and 29 show the considerable decreases in dynamic shear modulus with temperature; this is more marked in highly loaded compounds and with blacks having strong hardening properties.

(b) The energy loss at constant deformation is considerably lower at 100° than at 30° C. This is due to the drop in dynamic modulus with increasing temperature and to the loss decrease in percentage, owing to the recognized greater resilience at higher temperatures.

(c) The classification of the various blacks is quite different when considering the value K or the ratio $\frac{Kq}{\lambda}$. For instance, the hysteresis loss of P.1250 black is greater than that of EPC black at 30° C, but is the same at 100° C. The greater conductivity of the former, however, results in reduced heating compared with the latter. Practical temperature tests on samples stressed at constant deformation confirm the importance of the effect of conductivity, especially with highly loaded stocks.

(d) The energy loss at constant force decreases with increase in black loading, the rate of this decrease being different for relatively rough blacks, such as SRF and FT, than for finer and active blacks like P.1250 and EPC.

With this type of stress (constant force) P.1250 black seems to be the best from the point of view of temperature rise, but this is not equally true when considering only energy losses.

Substantially similar results are obtained also with GR-S rubber, less accelerated compounds being used with sulfur content of 1.7 per cent. The added sulfur does not alter the classification of the blacks, and leaves the absolute hysteresis values practically unchanged.

SUMMARY

Laboratory tests for evaluating energy losses due to hysteresis are analyzed. The importance of taking into consideration the thermal conductivity and cooling conditions of the rubber sample for the evaluation of heating due to hysteresis losses at temperature equilibrium is discussed.

Two new test methods, based on forced resonance oscillations, are described, in which the rubber samples are deformed respectively in shear and in tension at frequencies of 20 to 200 cycles per second, with dynamic shear strain of 0.02 to 0.4 and dynamic tension strain of 1 to 5 per cent, and at a temperature of 20 to 110° C.

Experimental results obtained with natural rubber and GR-S gum and tread stocks are presented. The hysteresis losses in gum stocks are found to follow the quadratic law *versus* dynamic shear strain, and the dynamic modulus G is found to be independent of shear strain. With tread stock the hysteresis losses are lower than would be the case with the quadratic law *versus* dynamic shear deformation, and the dynamic modulus G decreases with increasing dynamic shear strain.

Neither the hysteresis losses nor the modulus depend on the shape or size of the specimen. The modulus is found to be independent of frequency, while the hysteresis losses are found to increase proportionally with frequency.

As an application of the test method, results are presented of the effect of the quality and quantity of various types of carbon black on hysteresis heating of GR-S stocks.

ACKNOWLEDGMENT

The authors wish to thank L. Emanueli, to whom is due the principle of the test methods indicated above, and who also directed all the research work in this field. The permission of the Pirelli Company to publish these results is also greatly appreciated.

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[1] Dillon and Gehman, *India Rubber World* **115**, 61, 217 (1946); RUBBER CHEM. TECH. **20**, 827 (1947).

[2] The momentum impressed is measured by the current passing through the coil, and the relation between momentum and current is determined by calibration with direct current or by means of applied weights.

[3] The Hevea and GR-S gum stocks used for the test are understood to be carcass stocks.

[4] The compressive stress used for our tests was 0.044 kg. per sq. cm.

[5] In all our tests, the value of E was calculated as follows:

$$E = \frac{F/S_0}{\Delta l/l_0}$$

where F is the actual force (in kg.), S_0 is the original unstrained cross-section (in sq. cm.), Δl is the actual elongation (in cm.), and l_0 is the original unstrained length (in cm.).

A STUDY OF THE INCREASE IN TENSILE STRENGTH OF VULCANIZED RUBBER WHEN IT BEGINS TO AGE *

ROBERT JUDEINSTEIN

ÉTABLISSEMENTS BOGNIER ET BURNET, FRANCE

Most investigators who have studied the aging of vulcanized natural rubber and synthetic rubbers have reported that the tensile strength first increases, then decreases, and that the magnitude of this initial change depends on the nature of the vulcanizate and on its state of cure. For instance, Stevens[1] and Park[2] found that, from the standpoint of good aging, the best state of cure was one slightly below that which gave the maximum tensile strength immediately after curing, and that when aged naturally in storage, rubber-sulfur vulcanizates showed after one hundred and twenty-five days tensile strengths still above the original values of the fresh vulcanizates.

However, no really systematic investigation of this phenomenon has yet been reported, and authors have confined themselves merely to calling attention to the phenomenon.

In itself, this increase in tensile strength is in no way surprising because it would, *a priori*, be expected that vulcanization would continue at the beginning of aging and that this effect would outweigh the degrading effect of oxygen. But it can be shown that in many cases the tensile strengths which are attained during the early period of aging are higher than those which can be obtained by direct vulcanization to any state of cure; hence there is either some sort of change in the vulcanization phenomenon or some other factor is involved.

In view of this, it was decided to examine the phenomenon in more detail and to attempt to ascertain the causes which are responsible for the changes in tensile strength.

CHOICE OF MIXTURE AND DEMONSTRATION OF THE PHENOMENON

Since the magnitude of the changes observed depend on the nature of the vulcanizate, preliminary experiments were carried out to determine what would be the most suitable recipe to be used in the investigation. Accelerated aging tests carried out with various vulcanizates of the pure-gum type led finally to the adoption of the following mixture:

Smoked sheet rubber	100
Sulfur	3
Mercaptobenzothiazole	1
Stearic acid	1
Phenyl-β-naphthylamine	1
Zinc oxide	5

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 26, No. 3, pages 172–176, March 1949. According to a notation by the author, the time available for this work was limited; hence it is not so comprehensive as it would otherwise have been.

The optimum state of cure was considered to be the time of vulcanization at the particular temperature which resulted in the highest tensile strength, measured twenty-four hours after vulcanizing.

Since the state of cure played a part in the phenomenon, it was important to study the behavior of mixtures vulcanized for different times and at different temperatures. The temperatures chosen were 125°, 135°, and 145° C; the optimum cure was determined for each of these temperatures, and the tensile strengths were measured. The results are shown in Table 1.

TABLE 1

Temperature of vulcanization	Optimum time of cure (min.)	Tensile strength (kg. per sq. cm.)
125°	60	200
135°	20	190
145°	10	180

A series of vulcanizates was then prepared by curing the mixture at these three temperatures for four different lengths of time, so that undercured as well as overcured samples would be obtained.

30, 60, 90, and 120 minutes at 125°
8, 20, 30, and 40 minutes at 135°
5, 10, 15, and 20 minutes at 145°

Schopper test-rings cut from these vulcanizates were placed in a Geer oven at 70° C, and the mechanical properties were measured at the end of each two days. The results are shown in Figures 1, 2, and 3.

An examination of the curves in these diagrams shows that, in every case except the mixtures vulcanized 15 and 20 minutes at 145° C, there was an increase in tensile strength at the beginning of the aging period.

Furthermore, the lower the state of cure of any mixture originally, the higher was the absolute value of the tensile strength reached during the aging. Consequently the highest possible tensile strength for a given mixture was obtained when the mixture was vulcanized for a length of time less than that corresponding to the optimum state of cure, and was then heated for several days at a temperature below the temperature of vulcanization.

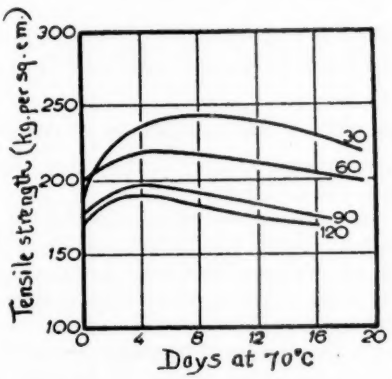

FIG. 1.—Aging curves of the mixture vulcanized at 125° C (the numbers represent the times of vulcanization in minutes).

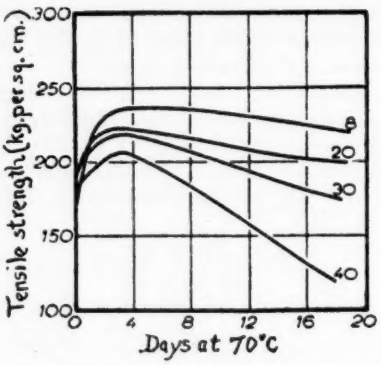

FIG. 2.—Aging curves of the mixture vulcanized at 135° C (the numbers represent the times of vulcanization in minutes).

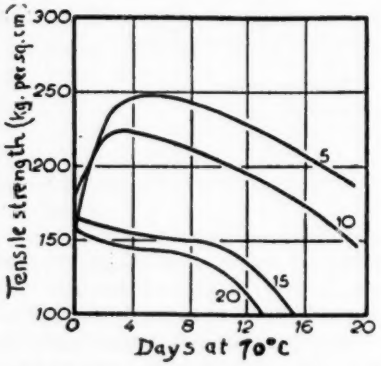

FIG. 3.—Aging curves of the mixture vulcanized at 145° C (the numbers represent the times of vulcanization in minutes).

On the other hand, the higher the temperature of vulcanization, the greater was the relative increase in tensile strength of the undercured mixtures, whereas the subsequent decrease in tensile strength on continued aging was much more rapid.

With respect to modulus and extensibility, the changes were similar to those in tensile strength, and the vulcanizates underwent in general the same relative change.

CHANGES IN THE PROPORTION OF COMBINED SULFUR

In view of the part played by sulfur in the vulcanization reaction, the first question which arises is the following.

Since the tensile strength curves cross one another, is this same characteristic to be found in the curves of combined sulfur; *i.e.*, does the sulfur which has remained free during vulcanization combine, during the oven heating, to a greater extent in the undercured mixture than it does in more highly cured mixtures? If so, do the points of intersection of the curves of mixtures having the same tensile strength correspond to the same percentage of combined sulfur? If not, is the sulfur which combines during the heating subsequent to vulcanization more active than that which has reacted during the original vulcanization process?

With a view to throwing light on this question, the following experiment was carried out. Two samples of the same composition as that of the preceding mixture were cured for 10 and 40 minutes, respectively, at 125° C (10 minutes corresponds to the time of setting, and 40 minutes to the optimum state of cure). These vulcanizates were then heated in a Geer oven at 70° C, and samples were removed at regular intervals to determine the tensile strengths and combined sulfur.

In determining combined sulfur, the method of Oldham, Baker and Craytor[4] was employed; this involves the determination of the free sulfur by conversion into sodium thiosulfate by heating with sodium sulfite, and calculation of the combined sulfur by difference between the total sulfur originally added and the final free sulfur.

The graphs in Figures 4 and 5 show tensile strength and percentage of combined sulfur as functions of the time of heating in the oven at 70° C. It will be seen that the tensile strength of the undercured mixture rapidly reached values which exceeded the tensile strength of the vulcanizates cured to its optimum state. On the contrary, although the percentage of combined sulfur in the undercured mixture increased appreciably, it did not reach the percent-

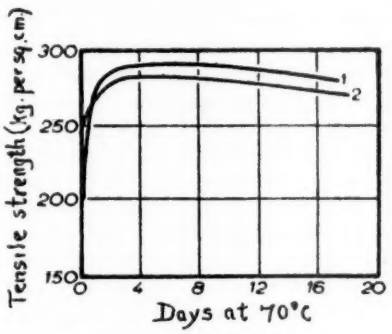

FIG. 4.—Tensile strengths of vulcanizates heated at 70° C.
(1) Undervulcanized mixture.
(2) Mixture cured to its optimum.

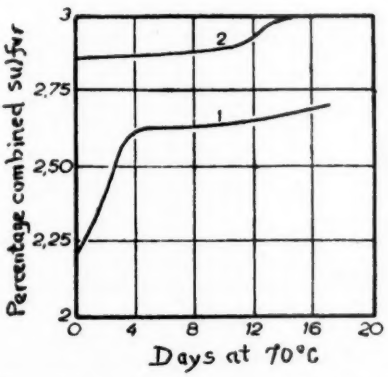

FIG. 5.—Combined sulfur as a function of the time of heating at 70° C.
(1) Undervulcanized mixture.
(2) Mixture cured to its optimum.

age of combined sulfur in the mixture which had been vulcanized to the optimum state of cure. Consequently the percentage of combined sulfur is not the determinant factor in the mechanical properties.

In addition to these experiments, some tests were carried out in which the samples were placed in sealed glass tubes in a vacuum of 10^{-3} mm. of mercury and then heated. These tests showed that the presence of atmospheric oxygen seemed to have some effect, not only on the tensile strength, but also on the combination of sulfur. Still another series of experiments was carried out in which oxygen was used in place of air, with a view to increasing the effect of the oxygen.

EFFECT OF HEATING IN OXYGEN

Two vulcanizates prepared under the same conditions as in the previous experiments were tested; test-specimens were placed, on the one hand in oxygen, on the other hand in a vacuum, in sealed tubes, which were then heated in a Geer oven at 80° C (this change in temperature was necessary because of problems connected with the equipment, but was of no significance as far as the object of the experiments was concerned).

The curves in Figures 6 and 7 show the values of the tensile strength and of the combined sulfur, respectively, as functions of the time of heating at 80° C. An examination of these curves leads to the following conclusions.

When the test-specimens were heated in the absence of oxygen, nearly all of the remaining free sulfur reacted, and the percentages of combined sulfur in the uncured mixture and in the mixture vulcanized to its optimum state became practically the same. On the contrary, when the test-specimens were heated in oxygen, much less sulfur combined during the heating. The apparent effect of oxygen was, therefore, to inhibit the combination of sulfur. Whatever the answer to the phenomenon, the percentage of combined sulfur in the undercured mixture remained lower than, or at the most equal to, that of the mixture which had been vulcanized to its optimum state of cure; moreover, the tensile strength increased to a higher value.

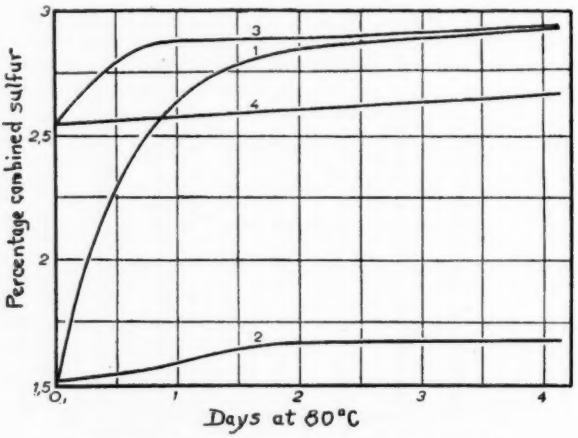

FIG. 6.—Tensile strengths of vulcanizates heated at 80° C.
(1) Undervulcanized mixture heated in a vacuum.
(2) Undervulcanized mixture heated in oxygen.
(3) Optimum-cured mixture heated in a vacuum.
(4) Optimum-cured mixture heated in oxygen.

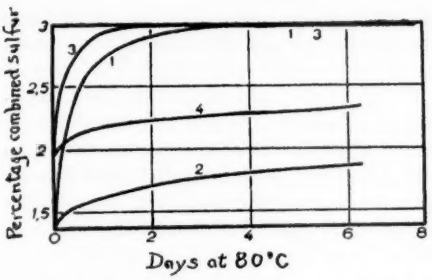

FIG. 7.—Combined sulfur as a function of the time of heating at 80° C.
(1) Unvulcanized mixture heated in a vacuum.
(2) Unvulcanized mixture heated in oxygen.
(3) Optimum-cured mixture heated in a vacuum.
(4) Optimum-cured mixture heated in oxygen.

In view of this, the percentage of sulfur which has combined is not in itself a governing factor in the tensile strength.

To throw further light on the factors responsible for this increase in tensile strength and in an attempt to differentiate between the part played by sulfur and that played by oxygen, recourse was had to the T-50 test. This test indicates the extent of network formation in a vulcanizate, irrespective of whether or not such a network structure is an effect brought about by combination of sulfur.

DATA OBTAINED BY THE T-50 TEST

It will be recalled that the T-50 test involves measuring the temperature at which a sample regains a predetermined part of its elasticity after it is stretched at room temperature, is then chilled to a temperature sufficiently low for the sample to lose its elastic properties, and finally is warmed gradually[5].

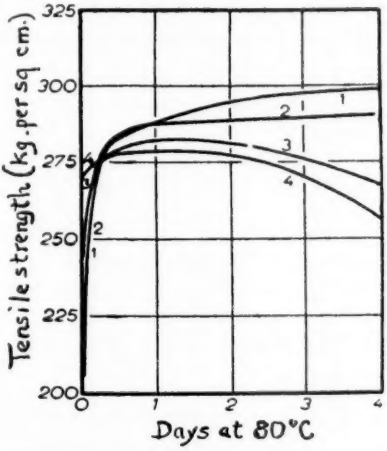

FIG. 8.—Tensile strengths of vulcanizates heated at 80° C.
(1) Unvulcanized mixture heated in a vacuum.
(2) Unvulcanized mixture heated in oxygen.
(3) Optimum-cured mixture heated in a vacuum.
(4) Optimum-cured mixture heated in oxygen.

A mixture identical with the preceding one was vulcanized for 7 minutes (time of setting) at 145° C and for 12 minutes (the optimum cure); the vulcanizates were then heated, on the one hand in a vacuum, on the other hand in oxygen, and the T-50 values as a function of the time of heating were determined. The results are condensed in the graphs of Figures 8, 9 and 10.

The curves representing tensile strength and combined sulfur confirm the general results of the preceding experiments (see Figures 6 and 7), any quantitative differences being due to the fact that vulcanization was carried out, for reasons of convenience, at 145° C, whereas in the earlier experiments it was carried out at 125° C.

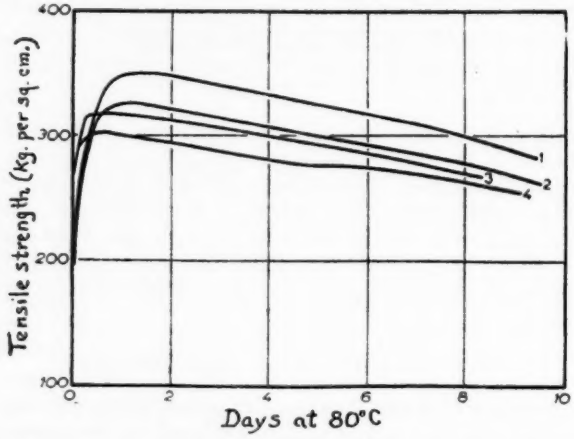

FIG. 9.—Combined sulfur as a function of the time of heating at 80° C.

(1) Undervulcanized mixture heated in a vacuum.
(2) Undervulcanized mixture heated in oxygen.
(3) Optimum-cured mixture heated in a vacuum.
(4) Optimum-cured mixture heated in oxygen.

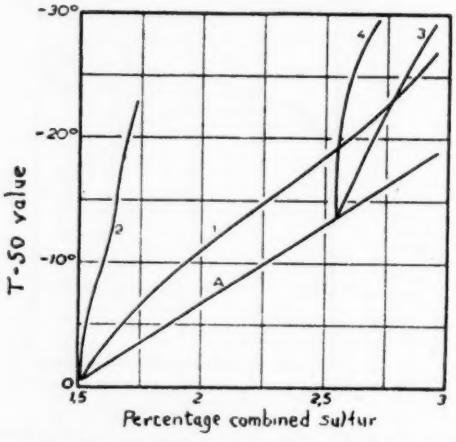

FIG. 10.—T-50 value as a function of combined sulfur during vulcanization (curve A) and during heating after vulcanization (curves 1, 2, 3, and 4).

(1) Undervulcanized mixture heated in a vacuum.
(2) Undervulcanized mixture heated in oxygen.
(3) Optimum-cured mixture heated in a vacuum.
(4) Optimum-cured mixture heated in oxygen.

The curve of the T-50 values as a function of percentage of combined sulfur is the most significant one; in fact, an examination of Figure 10 leads to some interesting conclusions.

First of all, when combination of sulfur has been brought about by vulcanization, the T-50 value is as shown by curve A, a linear function of the combined sulfur. This corroborates the observations of other investigators[5]. Turning now to the case where combination of sulfur is brought about by heating subsequent to vulcanization, the change in T-50 value is again practically a linear function of the combined sulfur, but the slope is noticeably steeper. This indicates that, for a given percentage of combined sulfur, the T-50 value is lower, *i.e.*, network formation is more extensive. This phenomenon is much more obvious in the case of the samples which were heated in oxygen. In this case it is logical to assume that it is the oxygen which contributes to the formation of a network and thereby improves the mechanical properties of the vulcanizate.

It is more difficult to explain the behavior of the samples heated in a vacuum. The fact should not be overlooked that, since the vacuum was not absolute, traces of oxygen present in the medium or dissolved in the rubber may have played a part in the phenomenon. Again, it is possible that sulfur which combines during heating in an oven after vulcanization is more reactive in some way, and forms more bridges of a new and different character, or effects some sort of rearrangement of the bridges already present. Probably both actions take place at the same time, but a more thorough study would be required to prove this with any degree of certainty.

The only reasonable conclusion at this time is that oxygen is a contributing factor in the increased network formation, that a certain amount of sulfur combines in addition to that already combined during vulcanization, and that these two phenomena together are responsible for the increase in tensile strength which results from moderate heating or by storage of vulcanized rubber.

CONCLUSIONS

In conclusion, the present study confirms the phenomenon of an increase in tensile strength at the beginning of aging. The magnitude of this increase depends on the nature of the acceleration and the state of cure; the tensile strength of an undercured sample increases much more than that of a sample vulcanized to its optimum state of cure, and the maximum tensile strength reached by the former is definitely higher than the maximum tensile strength reached by the latter. The phenomenon is therefore not simply postvulcanization.

This increase in tensile strength takes place in the presence of oxygen and also in a vacuum as high as 10^{-3} mm. In the latter case, measurements of the T-50 value and combined sulfur give indications of an increase in network structure for a given percentage of combined sulfur.

Oxygen is a contributing factor in increasing the network structure, but, in its presence, combination of sulfur is not so great and the maximum tensile strength attained is lower.

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PERMANENT SET IN VULCANIZED RUBBER *

L. MULLINS

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

The residual extension which remains after a sample of rubber has been stretched for some period, then released and allowed to recover, is popularly called permanent set. This set, however, is far from being permanent since it continuously decreases with the period of recovery; furthermore, after the rate of recovery has become exceedingly slow and is no longer readily observable, an increase in temperature will usually result in a sharp increase in the rate of recovery. It has been usual to identify this set with irreversible plastic flow, but it will be immediately evident that this can rarely be justified for, owing to incomplete high-elastic recovery, the measured value of set is a combination of both plastic flow and high-elastic deformation which has not completely recovered. Thus before any attempt is made to discuss the interpretation of the results of set tests, a study must be made of the significance of set.

Treloar[1] has investigated this phenomenon in raw natural rubber and has shown that entanglements or cohesional linkages may form while the rubber is stretched, and these oppose recovery; further, although van der Waals forces between the long-chain molecules largely control the rate and the amount of recovery, the crystallization of rubber produced by stretching may profoundly influence the set. On the other hand Tobolsky[2] has studied the set which results from stretching rubber vulcanizates at high temperatures; in such cases the amount of set is controlled by two processes which take place while the rubber is stretched; one of these involves the oxidative breaking of network chains, the other the oxidative cross-linking of network chains.

Although these ideas are well founded, they do not provide a completely satisfactory basis for the understanding of set, and the purpose of this work is to extend these ideas and to explain the significance of the results of normal set tests; in these tests rubber samples were extended at room temperatures to moderate elongations for relatively short periods of time. Most of the tests performed in this investigation were made on dumbbell shaped samples, which were extended by 200 per cent of their initial length for fifteen minutes at room temperature and then allowed to recover for one hour at room temperature; the residual extension was then noted and expressed as a percentage of the initial length. These tests will be referred to as normal set tests. In some tests various periods and temperatures of extension and recovery were used.

EFFECTS OF FILLERS ON SET

Normal set tests were made on a series of natural rubber vulcanizates including a pure-gum vulcanizate and others with similar volume loadings of a variety of fillers (approximately 20 per cent by volume). The compounding

* Reprinted from the *India Rubber World*, Vol. 120, No. 1, pages 63–66, April 1949. This paper was presented at the Rubber Technology Conference, London, June 24, 1948.

TABLE 1

COMPOSITION OF MIXINGS

Base mixing	(Parts by weight)
Smoked sheet rubber	300
Zinc oxide	5
Stearic acid	2
Sulfur	3
Mercaptobenzothiazole	0.8

Additional ingredients were as follows:

Mix A	None
Mix B	MPC black 50; pine tar 4.5
Mix C	FT black 50
Mix D	Activated whiting 75
Mix E	Colloidal china clay 75
Mix F	Magnesium carbonate 60
Mix G	Barytes 335

Vulcanized for 30 minutes at 153° C

details are given in Table 1; all mixes were cured to the optimum indicated by tensile tests. With the pure vulcanizate the set was extremely small, but with the loaded vulcanizates much larger values of set were recorded. Figure 1a shows the results of repeated normal set tests performed on samples from each mix; here, after the one hour's recovery of the previous test the samples were measured and extended again to the same final length. The figure does not show the results for the pure vulcanizate, which were always very small (<½ per cent). In all cases the results clearly show that after the first stretch the contribution of subsequent stretches to the set gets progressively smaller. Measurements were made also of the stress required to extend samples to the chosen elongation; the results are shown in Figure 1b. Here the stress required to extend the samples gets progressively smaller as the number of stretches increases. Comparison of the two sets of results shows that stretching results in little increase in the set when it does not also lead to softening. This phenomenon of softening which results from previous stretching has been discussed in an earlier work[3] and is attributed to a change in the disposition of the filler particles produced by stretching.

The results demonstrate also the differences which occur when changes are made in the type of filler; two important features are (1) those fillers which are

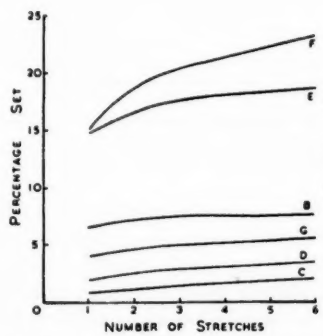

FIG. 1a.—Effect of repeated stretching on set.

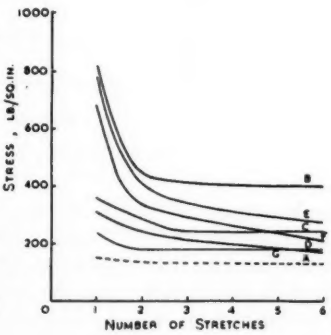

FIG. 1b.—Effect of repeated stretching on stiffness.

known to give anisotropic properties show greater set, and (2) the stiffness of the rubber is not a useful indication of the set to be expected when vulcanizates containing different types of fillers are compared. These features, which are shown clearly by the data in Table 2, will be referred to later in this paper.

TABLE 2

STIFFNESS AND SET AT 20° C

Filler	None	MPC black	Activated whiting	Colloidal china clay	Magnesium carbonate	Barytes	FT black
Stress (300%) (lbs. per sq. in.)	200	1580	420	870*	730*	335	600
Set (200%) (%)	0.5	7.5	2	13*	14*	4	1

* Measured along grain.

EFFECT OF TEMPERATURE OF RECOVERY ON SET

It is well known that samples retract continuously after release, and that an increase in the temperature of recovery leads to an increase in both the rate and extent of recovery. Samples which had been extended for fifteen minutes at room temperatures were allowed to recover at various elevated temperatures ranging from 20° to 120° C; at the highest temperatures the recovery was rapid and almost complete, showing that the amount of plastic flow or truly irreversible processes occurring during extension was very small.

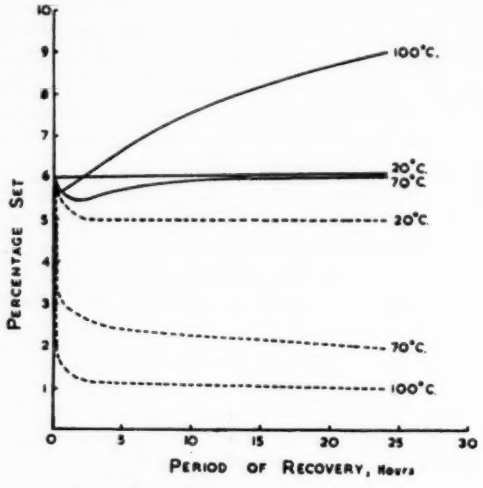

FIG. 2.—Recovery at various temperatures.

The broken lines in Figure 2 show the recovery with time of the MPC black vulcanizate at 20°, 70°, and 100° C; these curves show the continuous recovery with time and the increased rates which occur at higher temperatures. The full lines in this figure show the set present after a further normal set test had been performed on samples which had been allowed to recover for various periods. It should be remembered that if there had been no recovery, this additional set test would have resulted in but little increase in set (see Figure 1);

thus the increase produced by this test is associated with the recovery of the material toward its initial state.

It will be observed that after a few hours' recovery at 100° C the set actually exceeds the value recorded for the first stretch. This condition is attributed to the exposure at high temperatures resulting in a greater degree of filler structure than was present in the original material. To confirm this, samples were heated to 100° C for 24 hours before any testing; subsequent normal tests showed that the set resulting from a single test had increased from 6.0 to 8.5 per cent, and the stress required to stretch the rubber to 200 per cent elongation had increased from 830 lbs. per sq. in. to 1,100 lbs. per sq. in. On the other hand, pure vulcanizates showed no significant change of properties resulting from this heat treatment.

ANISOTROPY PRODUCED BY STRETCHING

Pronounced differences exist between the physical properties of vulcanizates containing fillers which stiffen the rubber before and after stretching. Stretching destroys much of the increase of stiffness produced by the filler; the softening is greatest in the direction of stretch. It seemed possible that these anisotropic properties of loaded vulcanizates, which are produced by stretching, may also be associated with set; to investigate this possibility repeated set tests were performed alternately in two perpendicular directions on sheets of rubber six inches square and one-tenth inch thick. The sheet was clamped along two opposite sides and extended so that the side of a one-inch square marked on the center of the sheet was extended 150 per cent (direction A); the sides were then held extended for fifteen minutes and allowed to recover for thirty minutes. The sides of the square and the thickness of the sheet within the square were then measured and expressed as a percentage of their value before any stretching. The next test was performed with stretch in the perpendicular direction (direction B). The result on two of the mixings is shown in Figures 3a and 3b.

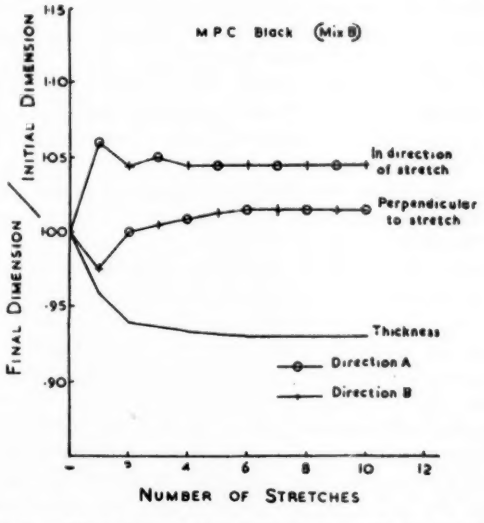

Fig. 3a.—Effect of repeated stretching in perpendicular directions.

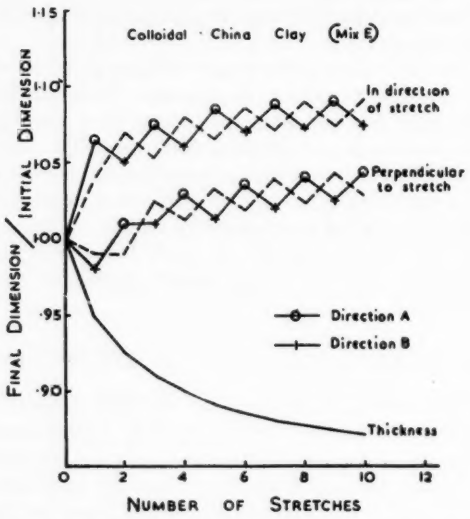

FIG. 3b.—Effect of repeated stretching in perpendicular directions.

First consider the results obtained on the MPC black vulcanizate. The set remaining after the initial stretch is accompanied by a reduction in the dimensions of the two perpendicular directions; the volume remains constant; the reduction in the direction in the plane of the sheet (direction B) is somewhat less than the reduction in the thickness, owing to constraints of the clamps causing less straining in direction B.

In the figures, measurements made in the direction of the initial stretch (direction A) are marked by circles; measurements in the perpendicular direction (direction B) are marked by crosses.

The second stretch, in the perpendicular direction (direction B), shows less set, owing to incomplete recovery after the first stretch. After several stretches these differences disappear, as there is then similar incomplete recovery of the previous stretches before every stretch. The results in Figure 3b were obtained on the colloidal china clay vulcanizate: besides showing behavior basically similar to that already discussed, they show also an interesting effect resulting from the presence of grain; the set in the direction of the grain is always greater than the set in the direction across the grain. In this figure the full and the broken lines represent cases where the initial stretch was made along and across the grain, respectively.

These results show that part of the filler structure associated with set can be oriented repeatedly from one direction to another; this reversal is shown clearly by the curves, after four or five stretches, in Figure 3a; they show also that any anisotropy of filler structure or grain, present before the commencement of the tests, is not destroyed by stretching to these elongations, *i.e.*, the differences between the set along and across the grain do not decrease. It appears that in loaded vulcanizates, which show true grain effects, the set can be considered to have two components, one due to the orientation by stretching of initially randomly disposed filler particles or chains of filler particles, and and the other due to grain or the preferential and apparently permanent orientation of the filler in one direction.

DISCUSSION

The results of these tests can be understood on the assumption that the most important single factor responsible for set, in normal set tests on loaded vulcanizates, is an anisotropy of disposition of the filler which results from stretching. "Pure" vulcanizates stretched to moderate elongations show very little set, and the difference between the set of a loaded and a pure vulcanizate is attributed to the orientation of anisotropic filler particles or of chains of filler particles in the direction of stretch. On release these particles are partially reoriented by thermal forces which tend to draw the rubber back to its original shape; this recovery of the rubber takes place in the face of energy barriers or weak bonds which can be ruptured readily by thermal forces resulting from increases in temperature. Thus the amount of set after a chosen period of recovery is dictated by both the increased rate of recovery which occurs at higher temperatures and the final equilibrium between these intermolecular bonds opposing recovery and the thermal forces leading to recovery. If large elongations are used, then crystallization may affect the set.

Of course, if extensions are carried out for long periods, or if they take place at high temperatures, then much of the set may be due to chemical processes which modify the rubber network. In such cases strong intermolecular bonds which cannot be readily ruptured by heating to higher temperatures are formed. Table 3 gives the set remaining after 24 hours' recovery at 120° C of samples

TABLE 3

PERCENTAGE SET AFTER 24 HOURS' RECOVERY AT 120° C

Period of extension at 20° C	Hours ¼	Hours 1	Hours 4	Hours 24	Days seven
"Pure" vulcanizate	0	0	0	0.5	1.0
MPC black vulcanizate	1.0	1.0	1.25	1.75	4.5

of both the pure and the MPC black vulcanizates, which had been extended to 200 per cent elongation for various periods at room temperature.

These figures demonstrate a progressive increase in the irreversible component of set with period of extension. Examination of recovery time curves, obtained on similar samples extended for various periods and allowed to recover at room temperature, showed that, although increased periods of extension caused greater set, they only slightly affected the rate of recovery expressed as a fraction of the set, and also the rate of recovery of the "pure" vulcanizate was much more rapid than that of the loaded vulcanizate.

Extension at high temperatures gave very large values of set, and a considerable amount did not recover after prolonged recovery at 120° C. In this investigation, however, we are restricting ourselves to a study of the set present after normal set tests, and it has been shown that processes of this type have little effect.

A possible contributing factor to the set of loaded vulcanizates, which was investigated, is that the volume of the compounded rubber may increase on stretching owing to the formation of vacuoles around the filler particles. Measurements of the change of volume produced by stretching to 200 per cent elongation made on all the vulcanizates, except the one including barytes, showed that in no case was the increase in volume greater than 0.1 per cent. Thus in these cases this factor was negligible.

Carbon black is by far the most important filler in the rubber industry, and a large range of grades is available for use as fillers; of these blacks, those with the smaller particle sizes stiffen the rubber more than those with the larger particle sizes, and electron-microscope studies of vulcanizates loaded with black show the presence of coherent contacting chains of spherical carbon particles; the chains are more prominent the smaller the particle size of the black; electrical measurements also show that chains must exist. On stretching, the increased stiffness produced by the incorporation of black is largely destroyed in the direction of stretch; and thus, other things being equal, the degree of anisotropy present after stretching is greater in samples containing the smaller particle-size blacks, which cause larger initial increases in stiffness. Table 4 gives measurements of the stress required to extend dumbbell-shaped samples of vulcanizates containing similar volume loadings (approximately 20 per cent by volume) of a variety of blacks together with the set remaining after normal set tests.

TABLE 4

STIFFNESS AND SET OF BLACK VULCANIZATES

Type of black	HMF	MPC	EPC	SRF	Lamp-black	MT	ET
Stress (300%) (lbs. per sq. in.)	2,200	1,580	1,550	1,420	1,380	750	600
Set (200%) (%)	7.5	7.5	7.0	4.0	4.0	2.5	1

The results show that those blacks which give the larger stiffness also result in greater set and therefore are in full agreement with the idea that set is due to orientation of anisotropic chains of carbon particles. Trends of this type have led to the use of empirical relations connecting stiffness or hardness with set, but close relations are not to be expected, for the amount of set results from the interplay of a number of factors which influence the energy barriers which have to be overcome during recovery; for example, different blacks or different fillers have different chemical natures which may in turn modify the formation of chains or intermolecular bonds. The differences which occur when changes are made in the type of filler are amply demonstrated by the results shown in Figure 1. One interesting feature of these results is that fillers known to possess anisotropic properties show large amounts of set, whereas fillers with spherical particles, which do not readily form chains, show little set; the degree of anisotropy of the filler particles or chains of filler particles is thus of considerable importance.

One important aspect of rubber compounding is the use of diluent materials to aid processing, to reduce the rubber content, or to soften the finished product. Materials included in this class may be complex mixtures ranging from thin liquids to pitchlike solids and may considerably affect the hardness, stiffness, and set of the vulcanized rubber. A survey of the results of tests done on a very wide range of materials shows that materials which harden and stiffen rubber normally cause increased set, whereas materials which soften the rubber normally cause a reduction in set. This conclusion appears at first sight to be analogous to the one just discussed, where an increase in stiffness produced by the filler was associated with increased set; however, the causes appear to be very different.

The presence of set after normal set tests is attributed to the slow rate of reorientation of anisotropic filler particles or chains and thus depends both on the degree of anisotropy and on how quickly the individual elements can swing

from biased to less biased positions. This rate is obviously controlled by the internal mobility, and the presence of diluent materials which modify this mobility affects the set. Increased internal mobility, besides producing more rapid recovery and less set, results also in a decrease in stiffness. Figure 4 shows the results of set and hardness tests of a control tire-tread type of mix diluted with a large variety of bituminous extenders; these results are explained adequately by this hypothesis, although it should be noted that the mobility which controls recovery is that existing after, and not before, stretching.

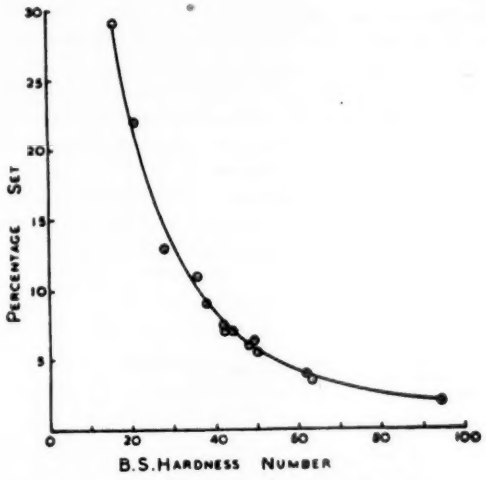

FIG. 4.—Effect of extenders on set and hardness.

Vulcanizates containing pitchlike extenders, which give high set and hardness at normal temperatures, show very much reduced set at elevated temperatures where the viscosity of the material is greatly reduced.

MEANING OF RESULTS OF SET TESTS

Probably the most popular use to which set tests have been put is for judging the state of vulcanization of rubber; a large amount of set is regarded as indicating plastic flow and undervulcanization, and a decrease in set with the suppression of plastic flow as due to cross-linking. Milled unvulcanized rubber is a mass of unconnected rubber chains and would not recover after stretching but for the fact that entanglements or intermolecular forces make the slippage of the chain molecules past each other slow and provide constraints which enable recovery to take place; the introduction of cross-links stops this slippage. This simple picture has resulted in considerable confusion in interpreting results of set tests and, more recently, the most important use of set tests has been in judging the snappiness, or the flow properties, of rubber vulcanizates.

It is often observed with loaded vulcanizates that although the set decreases rapidly during the early stages of vulcanization, it may pass through a minimum and thereafter increase instead of getting progressively smaller, or remaining very small; this minimum often occurs after short periods of vulcanization before other tensile properties have reached their optimum value. The evi-

dence which has been put forward here suggests that such minima are associated with a continuous aggregation of filler particles which occurs readily at the high temperatures used for vulcanization. This aggregation, besides producing increased stiffness, conductivity, and power factor, also leads to an anisotropy of the filler when its chains are oriented by stretching. The measured value of set is then a superposition of two components, one due to plastic flow, and the other due to orientation of filler chains. The first component decreases with increased periods of vulcanization; while the second increases. Thus normal set tests are often of no assistance in assessing vulcanization when loaded vulcanizates are employed. However, if the test samples were allowed to recover at elevated temperatures, the reorientation of the filler would be assisted, and the residual set would then measure plastic flow and therefore vulcanization; unfortunately the set to be measured would then be small.

It appears that normal set tests on loaded vulcanizates do not give a valuable indication of the flow behavior to be expected in service; for this purpose long-term set, creep, or stress relaxation tests are necessary. However, the set after extensions at high temperatures may be a useful accelerated test, for here the rate of the deteriorative chemical processes is increased, but, as in all accelerated tests which involve the interplay of a number of factors, the results must be used with caution.

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A SURVEY OF RESILIENCE AND THE DEVELOPMENT OF RESILIENT COMPOUNDS *

ROBERT F. SHAW

The replacement of natural rubber by synthetic elastomers has led to a search for a satisfactory resilient material from which to make packings for various hydraulic mechanisms.

This article covers the library research on resilience and incorporates the findings into actual test compounds and methods. Test data on these compounds are included, and they show the effects on resilience of the type of measuring instrument, of the temperature at which the measurements are made, and of compounding ingredients.

DEFINITIONS OF RESILIENCE AND RELATED TERMS

Resilience.—In a rubber or rubberlike body subjected to and relieved of stress, resilience is the ratio of energy given up on recovery from deformation to the energy required to produce the deformation. Resilience for these materials is usually expressed in percentage[54].

Hysteresis.—Hysteresis is the percentage energy lost per cycle or 100 per cent minus the resilience percentage[54].

Dynamic modulus.—The dynamic modulus is the ratio of stress to strain under vibratory conditions. It is usually expressed in lbs. per sq. in. for unit strain (dynamic spring rate)[54].

Damping.—Damping refers to the progressive reduction of vibrational amplitude in a free vibration system. It is the result of hysteresis, and the two forms are frequently used interchangeably[54].

Heat build-up.—This is a term applied to the increase in temperature of a rubber specimen when subjected to forced oscillation. The greater the hysteresis, the greater is the heat build-up.

Impact resilience.—Impact resilience is a function of internal friction (hysteresis effect) and dynamic modulus[50].

Resilience.—Resilience is a composite property which depends on hardness and internal friction[50].

Rebound.—This term indicates the percentage recovery of an object after it strikes the rubber specimen, or after a ball-shaped rubber sample strikes a hard surface.

Flexometer.—This term is applied to a machine which alternately subjects a rubber specimen to high-frequency cyclic compression, tension, shear, or torsional forces.

Resonant vibrator.—This is the high-frequency dynamic fatigue tester which subjects a rubber specimen to vibrational forces that produce the greatest amplitude of vibration when the system is tuned to its resonant frequency.

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METHODS OF RESILIENCE MEASUREMENT

Resilience methods and machines have been classified on the basis of the way in which the rebound or recovery is determined. These methods have been given in the literature[1,2,3], and are in general as follows:

- Impact Resilience
  - Free falling
  - Pendulum
- Free Oscillations
  - Torsion
  - Extension
  - Compression
  - Shear
- Forced Oscillations
  - Flexometers
  - Dynamic oscillators
    - Resonant frequency
    - Non-resonant frequency
- Other Methods

IMPACT RESILIENCE

Free falling

The simplest method of measuring resilience is the dropping of a ball-shaped rubber sample and noting the vertical rebound from a hard surface[8]. The opposite principle is employed by the elastomer of Breuil, which allows a falling metal ball to rebound off a rubber specimen, and the rebound read off the scale on the enclosing glass tube[8,55].

The falling ball test of Hock[8] measures the elasticity of rubber by the use of a metal ball falling on to a rubber specimen mounted on a slanting base and measuring the horizontal component of the rebound.

The Gaston falling ball resiliometer[4], Shore scleroscope[3,5], Williams elastometer[6], Bashore resiliometer[7], and St. Joe inclined-plane rebound tester[9] are all variations of the free falling method of determining resilience.

The Whitney rebound tester[10] indicates the percentage recovery of a spherical tipped metal weight sliding in a metal tube after being allowed to drop on a solid rubber object such as a solid rubber truck tire.

Pendulum

The principle of the pendulum hammer for measuring the elasticity of rubber was arrived at independently by van Itersen and Schob[8]. The Schob pendulum as manufactured by Schopper[11] was released from varying points on a sector, and the rebound determined by a pointer on a calibrated scale. A double-pendulum design was used to get the physical characteristics, since such a system prevented loss of stray energy as the rubber specimen was struck simultaneously from opposite sides[8].

The Lupke impact resiliometer is based on the rebound of a metal rod of known weight, suspended as a horizontal pendulum, after striking against a rubber specimen held on a rigid anvil. The resilience is the ratio of the returned energy to the impressed energy and is written as a percentage[13].

The Dunlop-Healy pendulum[12,39,57] is a metal pendulum whose energy is transmitted to a rubber test-block by a steel ball fixed to the leading edge. The displacement corresponding to the height from which it is dropped is measured along a horizontal scale.

The Healy-Goodyear pendulum[14,15,16] is a modification of the Dunlop-Healy, with the rebound indicated by an electrical device, and a deflection indicator added to measure the penetration of the hammer into the test block.

Modifications as to size, but using the same principle, is employed by the pendulums of Barnett and Mathews[17] and Goodwin and Park[18].

FREE OSCILLATION

Free-oscillation instruments produce damped cycles of impressed amplitudes on the rubber samples held in torsion, extension, compression, or shear.

Torsion

The Mooney and Gerke torsional pendulum[19,21] consists of a torsional pendulum mounted with a calibrated ring and supported entirely by the rubber specimen, which furnishes the restoring torque. The ratio of the damped amplitude to the impressed amplitude gives the resilience.

The Firestone autographic pendulum[20] is a torsion pendulum that scribes a damped sinusoidal curve at the natural frequency of the rubber compound.

Extension

The extension resilience device of Cassie, Jones, and Naunton[22] consists of a torsion head which, when rotated, alternately stretches and relaxes the rubber sample held in an oven between a fixed and a movable clamp.

Compression

The free oscillation apparatus of Naunton and Waring[23] measures the amplitude of a pendulum whose fulcrum is held between two compressed rubber specimens. The moment of inertia of the system can be varied by means of a movable weight on the pendulum arm, which has a pen on the end to record the amplitude.

The Harris pendulum[26] is a vertical weighted arm, suspended by the rubber sample, which oscillates against rubber pieces so that the rubber contributes to the damping action as well as the spring constant. The pendulum is set in free vibration, the frequency recorded, and the resilience calculated.

Compression and shear

The Yerzley oscillograph[24,25,54] consists of a balance beam supported at its center by knife edges. The test-specimen, which may be in compression or in shear, is placed between loading platens off center of the beam and is supported by another knife edge and a stabilizing arm. The balance beam is loaded with standard weights to cause an unbalanced condition; the arm is released, and the cycling of the arm, as the rubber is alternately compressed and released, is recorded by means of a pen on a chronograph. The resilience, in percentage, is defined as the vertical height of the rebound of the first cycle divided by the preceding height of fall and multiplied by 100. Values are reported for only the weight that causes a static compression of 20 per cent.

FORCED OSCILLATIONS

Flexometers

The Firestone flexometer, as described by Cooper[27], measures the heat build-up of a compressed rubber specimen under load when rotated off center between a stationary and a moving platen. The time required to "blowout" due to the heat generated at a given speed, off center distance, and loading is

an indication of the hysteresis and indirectly a measurement of resilience, since 100 per cent minus the hysteresis or energy loss gives the resilience.

The St. Joe flexometer[28] is a modification of the Firestone flexometer, and also measures heat build-up.

The Goodrich flexometer[29] measures the temperature rise of a compressed rubber sample when subjected to high-frequency cyclic compression of definite amplitude.

The Roelig dynamic fatigue tester[30] can be used in tension, tension-compression, or compression. The amplitude of the oscillation is measured, and the dynamic hysteresis loop is given by a mirror mounted on the mechanism which reflects a light onto a screen, and the image produced is photographed.

The Martens compressed ball rolling test or crushing tester[31] consists of two parallel circular iron plates; the upper is a driven rotating pulley; the lower is stationary, and has a V-shaped groove in which a solid rubber test ball is rolled. The upper plate is rotated, and the blow-out temperature is recorded, or the inner temperature of the ball is determined after a definite rolling time.

Dynamic oscillators

The high-frequency dynamic fatigue tester of Naunton and Waring[32] determines the modulus and resilience of rubber in compression when electrically driven at its resonant frequency. The forced oscillations produce the greatest amplitude of deflection at resonance, which is obtained by adding weights to the vibrating member.

The Kosten compression method[33] measures static and dynamic properties of rubber under compression by steel springs, when confined by steel plates and subjected to vibrational forces of known magnitude and frequency below the resonance value.

The Goodyear forced resonance vibrator of Gehman, Woodford, and Stambaugh[34] deforms rubber in compression at the resonant frequency and enables the dynamic modulus to be determined by the amplitude of vibration. The method is similar to that of Naunton and Waring.

The Gehman forced resonance vibrator[35] is modified to test-specimens in tension, compression, shear, or torsion under various superimposed static stresses.

The Gehman, Jones, and Woodford vibrator[36] is a variation of the Goodyear oscillator and vibrates at 60 cycles per second.

The Firestone forced resonance shear vibrator[2] deforms rubber at frequencies of 20 to 20,000 cycles per second, depending on the resonant frequency. The shear method is the most satisfactory, since it eliminates any differences as to the size and the shape of the sample.

The Buick dynamic tester[37] is composed of a mechanical stroker, an electronic strain recorder, and a photographic recorder. It measures the hysteresis and damping rate of rubber held in tension compression or shear loading. Static tests and three dynamic tests are possible: (1) constant-speed tests; (2) constant temperature; (3) endurance tests.

The vibrator of Moyal and Fletcher[38] employs an electrically driven oscillator which drives a steel bar with the rubber in compression in the center. The mechanical resonance of the system is found by observing the vibration of a point on the bar with a microscope.

The rotating unbalanced weight vibrator of Fletcher and Schofield[38,44] utilizes an inertia-type piezo-electric pickup to record the amount of vibration caused by the unbalanced rotating member.

The Linhorst shear resiliometer[45] measures the amount of vibration transmitted through a mounting under varying temperature conditions by measuring the applied amplitude of vibration compared with the transmitted amplitude.

OTHER METHODS

The Shore elastometer[48] yields a surface measured elasticity by subjecting the rubber to the semisharp penetrator point and reading the percentage recovery when the indicator hand is released.

The Taber stiffness gage[49] expresses resilience as the ratio of normal stiffness to initial stiffness, where the normal stiffness is defined as the loss in stiffness due to fatigue as determined on the gauge.

FACTORS AFFECTING RESILIENCE

- Measurement
  - Duration of loading
  - Preworking
  - Temperature
  - Magnitude of the stress
  - Method of stress application
  - Amplitude of the deformation
  - Energy losses other than in the rubber
  - Frequency
- Sample
  - Shape
  - Thickness
- Material
  - Elastomer
  - Fillers
  - Plasticizers
  - State of cure

MEASUREMENT

Duration of loading

The resilience may vary with the duration of deformation of the period of contact, and this variation is most marked when the period during which the rubber being deformed is comparable to the orientation time, since this short duration of deformation causes little energy to be lost in irreversible viscous flow[60]. Resilience falls markedly with decreasing time of contact or decrease in ball size[61].

Preworking

Striking or flexing a rubber sample repeatedly increases the resilience to a constant value[13,14,19,25]. In all cases several cycles of loading and unloading should be performed before resilience readings are taken.

Temperature

The resilience of rubber samples is influenced both by the ambient temperature and the equilibrium temperature characteristic of the measuring instrument[3].

Resilience increases with increased temperature, and the rate of increase varies for different elastomers[6,8,14,15,19,21,22,35,41,42,44,45,52,56,59,62].

Resilience decreases with lowered temperatures to a minimum, then increases somewhat with a further drop in temperature[56].

Instruments of the dynamic type increase the temperature of the specimen and give correspondingly higher values. Therefore comparable results are obtained by having a standard specimen temperature preferably equivalent to service temperature and not ambient temperature[3].

Magnitude of the stress

Resilience may be either increased or decreased as a result of increasing the magnitude of the applied stress. If impact energy is increased by increasing the mass of the striking body, the resilience increases. If the energy is increased by increasing the height of the drop, the resilience is decreased[1,8,13]. Increased inertia of impact increases resilience, and increased velocity of impact decreases resilience when the Yerzley oscillograph is used[3].

Method of stress application

The type of applied stress affects resilience. Results are comparable only if measured in the same way, *i.e.*, compression tension, torsion, or shear with the latter giving the highest values and being the most reliable[2,3,60].

Amplitude of the deformation

The nonlinear stress-deformation curve of rubber leads to a dependence of the apparent elastic modulus on the actual value of the stress. The resilience then varies with the applied stress and in a complimentary way with the amplitude of deformation[60]. This factor is dominant in instruments of the forced oscillation type. The effect of amplitude is not more than 2 or 3 per cent in the Naunton and Waring oscillator[23].

Energy losses other than from the rubber itself

The energy losses at the front and the back surfaces of the rubber sample are increased if bloom, chalk, or rubber dust are present[8,43].

The effect of windage or air damping in the pendulum type is less than 1 per cent, but the effect of shuffle or movement of the specimen can amount to up to 4 per cent[17,25,43]. Shuffle increases with pendulum energy and depth of impact and, in general, increases with increase of resilience.

The friction of the testing machine as well as vibration tends to lower resilience values.

Frequency

Resilience decreases when the frequency is increased[2,23,26,34,61]. This change may amount to 5–15 per cent when the frequency is increased several hundred cycles. Resilience reaches a maximum at some intermediate low frequency. It is best measured at the resonant frequency in forced oscillation tests, since the amplitude is greater.

SAMPLE

Shape

The area of the rubber test-specimen has little effect on resilience[8]. The shape of the sample in dynamic forced-oscillation tests affects the resilience, since the whole sample is subject to vibration. Similar shapes should have the same form factor, and the results of samples deformed in shear should be independent of the sample[2,60].

Thickness

The thickness of the test-specimen affects resilience most in the impact tests. If the ratio of the penetration to the thickness is high, the resilience is decreased. Resilience increases with decreased sample thickness up to ½-inch and then becomes constant[7,8,13].

MATERIAL

Elastomer

The type of elastomer used in a compound determines the limits of resilience, since all other factors except temperature affect this property evenly for different materials. Natural rubber has the least change in resilience over the temperature range 32 to 212° F, with Neoprene-GN, GR-S, Buna-N, and Butyl, following in that order[41,62,53]. Polymers high in butadiene content exhibit a minimum change in resilience over the range 32 to 212° F. When a portion of the butadiene is replaced with styrene or acrylonitrile, the low-temperature resilience properties are impaired. However, acrylonitrile definitely contributes to improved resilience at elevated temperatures[62].

Room-temperature resilience ranks the various elastomers in the order shown in Table 1[20,50,62].

Fillers

The effect of adding reinforcing agents or fillers to various elastomers is in each case to reduce the resilience. Pure-gum stocks have the highest resilience, and resilience decreases directly as the percentage of filler is increased. In the case of carbon blacks, for equal loadings, the coarser carbons produce less change than the finer carbons[15–17,40,46,47,51,61].

With increased loadings of carbon black, resilience properties of natural rubber and Neoprene become more sensitive to temperature[51].

Plasticizers

The type and the proportion of plasticizer used in a rubber compound affect resilience. The use of the smallest amount of a compatible softener aids resilience[63,64,65]. Good softeners are tributyl phosphate, dibutyl phthalate, and dibutyl sebacate.

Softeners aid resilience at low temperatures since the hardness is reduced.

State of cure

Resilience does not vary with time of vulcanization beyond the optimum cure[41,62]. This optimum cure, however, is usually longer or is a decided overcure in regard to other properties such as tensile and elongation[64].

The resilience of GR-S and natural rubber are affected by the sulfur content of the compound. If the sulfur content is increased more than 3 per cent, the stock becomes more temperature-sensitive[62].

In compounding, retarding materials should be avoided, and the acceleration increased to obtain "a tight cure", which enhances resilience[63,64,65].

EXPERIMENTAL PROCEDURE

TEST METHODS

The following ASTM test methods were used in carrying out the experimental work in this program.

D15–41—Preparation of sample for physical testing.
D412–41—Tension testing of vulcanized rubber.
D573–45—Aging, accelerated oven method.
D314–39—Hardness of rubber.
D395–40T—Compression set of vulcanized rubber.
D471–46—Changes in properties of rubber and rubberlike materials in liquids.
D736–43T—Brittleness, low temperature.

Since there is no standard test method for determining resilience, the methods of Lupke and Yerzley were used.

The apparatus of Lupke was constructed in accordance with measurements given on pages 296–297 of the "Vanderbilt Handbook" (1942), and is shown in Figure 1.

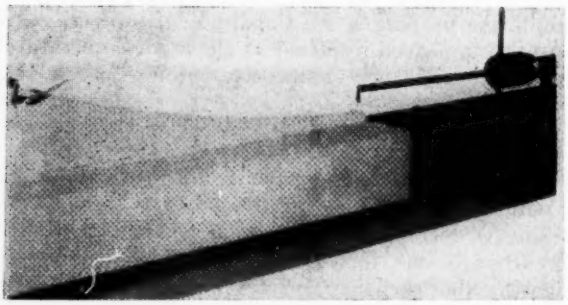

FIG. 1.—Lupke resiliometer.

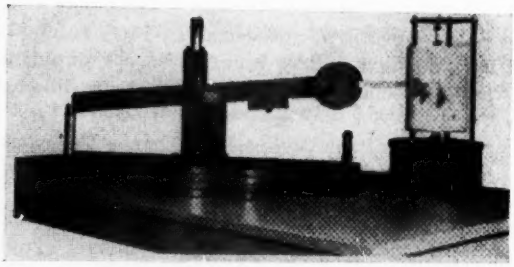

FIG. 2.—Yerzley oscillograph.

The Yerzley oscillograph, as manufactured by the American Instrument Co., and as shown in Figure 2, was also used. The proposed ASTM standard[54] was followed in using the Yerzley oscillograph, and measurements were made in a constant temperature-humidity room at 70° F and 50 per cent relative humidity.

M-1 SERIES OF COMPOUNDS

Since Neoprene was reported to have the highest resilience of all types of synthetic rubber, this material was used as the basis for the experimental compounding. The M-1 series was designed to show the effect of the various

classes of carbon black when used in the amount of 15 parts per 100 of Neoprene. The types of carbon blacks, based on particle size, were represented starting with the (MT) medium thermal furnace black, which is the coarsest commercially available carbon black, and continuing through decreasing particle size carbons to (CF) conductive furnace carbon black. Another class of carbon black: namely, channel black, was not included in this study because of its adverse effect on resilience due to fineness of particle size.

M-2 SERIES OF COMPOUNDS

The M-2 series was designed to show the effect on resilience of increased loading of carbon black on a Neoprene compound. Thermax, which is a medium thermal carbon of large particle size, was used, since carbons of this type decrease resilience the least. The proportions used were 15, 25, 35, 45, and 55 parts per 100 of Neoprene.

The development of resilient compounds was the major goal of this study, but other physical properties commonly used in evaluating rubber compounds were also determined. These properties include tensile strength, elongation, hardness, compression set, deterioration due to air-oven aging, change in properties due to oil immersion, low-temperature flexibility, and mold shrinkage.

RESULTS OF EXPERIMENTS

The inherent resilience of various elastomers, as gathered from the literature, is shown in Table 1. The values shown are the maximum attainable for the given polymer when tested by the rebound method at room temperature.

The M-1 series of compounds is shown in Table 2. The following results are shown in this table.

TABLE 1

INHERENT RESILIENCE OF ELASTOMERS

Per cent recovery (room temp.)	Elastomer
100	
95	
	Natural rubber
90	
	Neoprene
85	
	Thiokol-ST
80	
75	
	GR-S
70	
	Buna-N (low acrylonitrile)
65	
60	
55	
50	
45	
	Buna-N (high acrylonitrile)
40	
35	
	Butyl
30	

TABLE 2

PHYSICAL PROPERTIES M-1 SERIES

Compound no.	M1	M1F	M1F1	M1F2	M1F3	M1F4	M1F5	M1F6
Original								
Class of carbon black	MT	FT	SRF	HEF	HMF	ACET	FF	CF
Name of carbon black	Thermax	P-33	Gastex	Sterling K	Philblack A	Acetylene	Statex B	Statex A
Cure time (min. at 307° F)	25	25	25	25	25	25	25	25
Tensile (lbs. per sq. in.)	3000	2550	2680	2710	2750	2720	3040	2930
Elongation (%)	925	935	840	865	835	885	880	920
Shore hardness	46	46	53	52	53	56	50	50
Lupke rebound	73	72	67	66	64	63	65	66
Yerzley resilience at 20% compression	80	79	72	72	70	69	70	71
Compression set (ASTM Method A)	8.8	8.8	8.7	7.9	8.7	7.5	9.1	10.7
Aging Tests								
Air oven (70 hrs. at 212° F)								
Tensile (lbs. per sq. in.)	2175	2165	2150	2315	2490	2405	2675	2875
Elongation (%)	795	775	800	800	755	810	820	845
Shore A hardness	50	50	50	51	53	55	52	54
808 Oil (7 days at 158° F)								
Tensile (lbs. per sq. in.)	2085	2040	2110	2150	2235	1975	2140	2175
Elongation (%)	740	745	750	750	770	680	775	720
Shore A hardness	38	39	40	41	42	41	40	38
Swelling Tests								
ASTM No. 1 (% weight)	−3.1	−2.9	−2.8	−2.8	−3.1	−2.5	−3.1	−3.5
% volume	−3.3	−4.2	−2.7	−2.8	−2.7	−2.1	−2.4	−3.5
U.S. Army Spec. 2–132 recoil oil								
(% weight)	14.9	13.6	13.9	14.6	14.1	14.7	12.6	15.1
% volume	25.8	23.4	23.7	24.4	28.9	26.3	29.4	28.2
SR-10 (% weight)	10.2	11.9	13.9	13.3	12.6	13.0	11.8	14.6
% volume	31.9	26.5	30.7	28.5	27.6	28.3	27.0	30.0
SR-6 (% weight)	91	89	94	89	92	85	91	91
% volume	150	149	115	152	153	147	152	155

The Lupke rebound decreases as the carbon black particle size decreases.

The Yerzley resilience decreases as the carbon black particle size decreases.

Hardness increases with increased carbon fineness.

The Yerzley resilience values average six points higher than the Lupke.

The following results are obtained from the data shown in Table 3 on the M-2 series of compounds.

The resilience values have been increased six points by changing the accelerators and the antioxidants to the M-2 formulation for equivalent carbon loadings.

TABLE 3

PHYSICAL PROPERTIES M-2 SERIES

Compound no.	M2	M2F	M2F1	M2F2	M2F3
Original Tests					
Parts Thermax	15	25	35	45	55
Cure time (min. at 307° F)	25	25	25	25	25
Tensile (lbs. per sq. in.)	2080	1952	1986	1840	1724
Elongation (%)	750	730	720	700	570
Shore hardness	54	55	56	60	62
Lupke rebound	78	77	76	75	72
Yerzley resilience at 20% compression	86	85	83	82	79
Compression set (ASTM Method A)	6.2	5.3	5.3	4.8	4.4
Flexible at ° F	−65	−65	−65	−65	−65
Mold shrink (inches/inch)	.024	.023	.022	.021	.020
Aging Tests					
Air oven after 70 hrs. at 212° F					
Tensile (lbs. per sq. in.)	1676	1530	1653	1683	1745
Elongation (%)	570	500	503	403	380
Hardness	58	60	62	66	70
808 Oil immersion (7 days at 158° F)					
Tensile (lbs. per sq. in.)	1550	1750	1800	1730	1660
Elongation (%)	620	650	660	650	520
Hardness	47	46	48	50	51
Swelling Tests					
ASTM No. 1 (% weight)	−3.2	−2.2	−2.8	−1.2	−1.2
% volume	2.8	1.1	−3.4	−4.6	−1.1
808 Oil (% weight)	15.0	13.0	13.0	11.6	11.6
(Recoil) % volume	17.2	19.0	11.0	19.0	7.5
SR-10 (% weight)	18.0	13.0	17.0	11.6	11.0
% volume	36.0	30.0	30.5	33.8	23.0
SR-6 (% weight)	62.5	62.0	57.0	46.0	43.0
% volume	93.0	65.0	65.0	50.0	40.0

Tensile strength decreases with increased loading.

Percentage elongation decreases with increased loading.

Lupke rebound decreases with increased loading.

Yerzley resilience decreases with increased loading.

Compression set decreases with increased loading.

Mold shrinkage decreases with increased loading.

Oil swelling decreases with increased loading.

Shore hardness increases with increased loading.

All compounds are flexible at −65° F.

Table 4 presents comparative data on compounds suitable for use as packings. Natural-rubber stock No. 34 has been in service for the past ten years.

TABLE 4

COMPARISON OF COMPOUNDS SUITABLE FOR FLOATING PISTON PACKINGS IN RECOIL MECHANISMS

	407 (M2F3)	407F	No. 34
Polymer	Neoprene	Neoprene	Natural
Type carbon black	Thermax	Gastex	Gastex
Class carbon black	MT	SRF	SRF
Parts carbon black	55	55	40
Parts mineral filler	0	0	106
Cure time (min. at 307° F)	25	25	18
Original			
Tensile (lbs. per sq. in.)	1724	2410	1850
Elongation (%)	570	400	430
Shore hardness	62	70	68
Lupke rebound	72	69	62
Yerzley resilience	79	76	69
Compression set (ASTM method A)	4.4	4.0	2.6
Low temperature flexibility at ° F	−65	−65	−75
	70 hrs. at 212° F		7 days at 158° F
Aging Tests			
Tensile (lbs. per sq. in.)	1745	2182	1810
Elongation (%)	380	227	330
Shore hardness	70	81	73
Corrosion Tests			
10 days at 158° F against silver	OK	OK	Tests not made
Steel	OK	OK	Service OK

Compounds 407 and 407F have higher resilience values at comparable hardness than the natural rubber compound. This condition is due to the fact that the rubber compound has a high loading of mineral filler, which reduces the resilience. With proper compounding, the natural-rubber stock could be made to have higher resilience than the Neoprene.

TABLE 5

COMPOUND FORMULATIONS

	M-1	M-2	No. 34
Neoprene GR-M 10	100	100	...
Pale crepe	...	...	100
Light calcined magnesium oxide	7	7	...
Zinc oxide	1.5	1.5	44
Phenyl-α-naphthylamine	...	2	...
Phenyl-β-naphthylamine	2	...	1.5
Para-phenylphenol	...	1	...
Di-ortho-tolylguanidine salt of dicatechol borate	...	2	...
Di-ortho-tolylguanidine	2	...	...
Mercaptobenzothiazole	...	...	1
Tetraethylthiuram disulfide	...	...	5
Tellurium	...	...	2.5
Stearic acid	0.5	0.5	1.5
MF carbon black	15	15	...
SRF carbon black	...	...	42
Whiting	...	...	62
Paraffin	...	...	1.5
Dibutyl sebacate	10	10	...
Cure min. at 307° F			
0.080-inch test pad	25	25	18
0.500-inch button	45	45	30

Other physical properties of the Neoprene compounds are equal or superior to the natural rubber compound. The only exception to this statement is that the natural-rubber compound has slightly better low-temperature flexibility. The aging values show the Neoprene to be better for high-temperature service, since natural rubber does not age well at temperatures up to 212° F.

Compound formulations of the mixes tested are shown in Table 5. The M-1 is the parent batch of the first series which features eight classes of carbon blacks as shown in Table 2. The M-2 is the parent batch of the second series, which features increased carbon black content, as shown in Table 3.

TABLE 6

PARTICLE SIZE OF CARBON BLACKS

Classification	Symbol	Diameter millimicrons
Medium thermal	MT	250–500
Fine thermal	FT	150–200
Semireinforcing furnace	SRF	70–90
High elongation furnace	HEF	60–70
High modulus furnace	HMF	50–60
Acetylene	Acet.	43
Fine furnace	FF	36
Conducting furnace	CF	36
East processing channel	EPC	30–33
Medium processing channel	MPC	25–30
Hard processing channel	HPC	20–25
Conductive channel	CC	10–20

Table 6 shows the classification of carbon blacks by particle size. The thermal, furnace, and acetylene carbons were the only type tested, since channel carbon blacks produce low resilience.

SUMMARY

A study was made of the methods and machines used in measuring resilience and classified as of the impact, free oscillation, forced oscillation, or other type. A search of the literature revealed that resilience is affected by numerous factors, such as temperature, duration of loading, magnitude of stress, method of applying stress, amplitude, frequency, and energy losses during measurement; by shape and thickness of the sample, and by the state of cure, amount and type of plasticizer, amount and type of fillers, and the type of elastomer used.

A series of Neoprene compounds was compounded, cured, and tested to determine the effect of various classes of carbon black on the resilience of the Neoprene elastomer, which is the most resilient commercially made rubber material. The resilience was found to decrease as the carbon black particle size decreased.

A second series of compounds utilizing 15, 25, 35, 45, and 55 parts of medium thermal carbon black based on the Neoprene were tested, and the results show that resilience decreases with increase in loading.

A comparison of the physical properties of these compounds with those of the currently used natural-rubber packing shows that the former are superior for replacing the natural rubber in mechanisms.

The Neoprene compounds possess better tensile strength, elongation, resilience, aging, and oil resistant properties than the rubber compound, but are slightly inferior in low-temperature flexibility.

ACKNOWLEDGMENT

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ENERGY OF RESILIENCE AND ABRASION RESISTANCE

A COMPARISON OF RECLAIMED AND CRUDE NATURAL RUBBER*

F. N. UPHAM

When laboratory-machine tests on rubber were first introduced as a routine procedure, the only tests made were the elongation and tensile at break. Later, the tests were extended to the measurement of the amount of work done in stretching and breaking the test-specimen, and the computation was based on the area under the stress-strain curve.

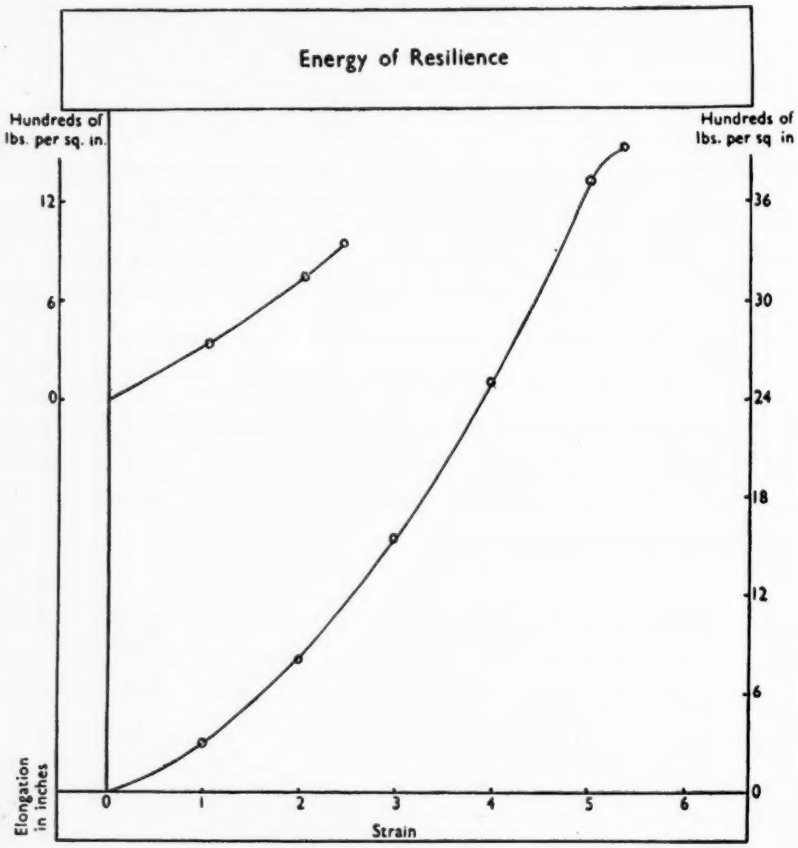

FIG. 1.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 24, No. 4, pages 196–198, December 1948.

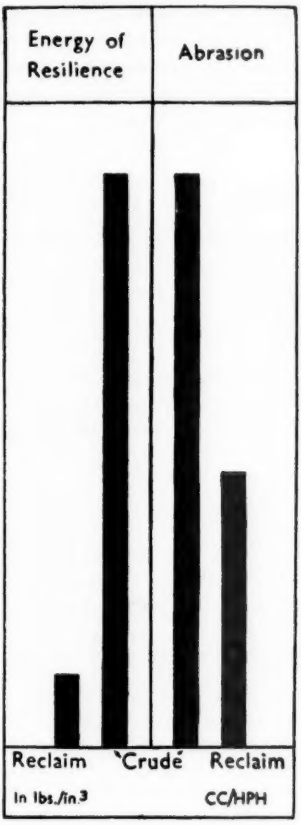

FIG. 2.

When stress-strain curves made in the above manner for reclaimed and crude rubber were compared, it was found that the reclaimed area was much smaller than that for new rubber. As an example of this difference, two curves are given here in which the areas are in the ratio of 682/85.

If the service given by the reclaimed rubber was in the same ratio as the areas, it is doubtful if the products made from it would have been satisfactory.

In view of the above, and because reclaimed rubber has always been used in the industry, it was thought that there must be some other property of reclaimed rubber which would not show as much difference from crude rubber as do the stress-strain curves. It is shown here that abrasion resistance is such a property, and that the ratio of the two abrasions is 513/248.

A graphical comparison of both stress-strain and abrasion resistance properties is shown in Figures 1 and 2. In the bar charts (Figure 2) for energy of resilience, the bars have the ratio 682/85. The bars of the abrasion resistance represent the reciprocals of the abrasion loss per horse-power hour, *i.e.*: $\frac{1}{248}$ and $\frac{1}{513}$. This is done to give the better stock the longer bar.

By comparing the results of the stress-strain and abrasion data, it is seen that if the service rendered was in the ratio of the respective areas, the crude rubber would give eight times the service of the reclaimed rubber, but if the service was in the same ratio as the abrasion resistances, the crude would give twice the service of the reclaimed rubber.

Natural Rubber
Stress-strain

Elongation (in.)	Tensile strength (lbs. per sq. in.)
1	300
2	800
3	1,550
4	2,500
5	3,750
5.3	4,000

Reclaim Rubber
Stress-strain

Elongation (in.)	Tensile strength (lbs. per sq. in.)
1	350
2	700
2.4	920

Abrasion resistance

248 cc. per h.p.h. for crude rubber
573 cc. per h.p.h. for reclaimed rubber

FORMULAS

Reclaimed rubber (d. 1.22)	170
Sulfur	3
Zinc oxide	6
Mercaptobenzothiazole	0.75

Natural crude rubber	100
Sulfur	3
Zinc oxide	6
Mercaptobenzothiazole	0.75
E.P.C. black	45.25
Stearic acid	2.5

The stress-strain data were obtained with a Scott Tester, the abrasion data with a Williams abrader.

VULCANIZATION AT HIGH PRESSURES *

C. S. WILKINSON, JR., AND S. D. GEHMAN

GOODYEAR TIRE & RUBBER COMPANY, AKRON 16, OHIO

Physical investigations employing high pressures have been carried out on many materials and systems. The development of the specialized techniques and the results obtained have been reviewed by Bridgman[1]. Work is described utilizing pressures as high as 1,500,000 pounds per square inch and, under very limited circumstances, up to 6,000,000 pounds per square inch. Most of the work was concerned with volumetric changes due to high pressure, phase transitions, and effects of pressure on physical properties such as viscosity, elastic constants, electrical resistance, and specific heat.

Rubber has been the subject of a number of high-pressure studies. The compressibility was determined by Adams and Gibson[2] for pressures up to 174,000 pounds per square inch. More recently, Bridgman[3] has reported volume changes for fourteen natural and synthetic rubber compounds for pressures up to 356,000 pounds per square inch. Figure 1 is a plot of Bridgman's data for Hevea gum and tread stocks. It is Bridgman's observation from the behavior of rubber packing washers that they tend to become brittle and crack under such high pressures. Scott[4] measured the effect of moderate pressures on the compressibility and electrical properties of rubber-sulfur compounds and showed that the compressibility increased at high temperatures but that this dependence on temperature diminished at higher pressures.

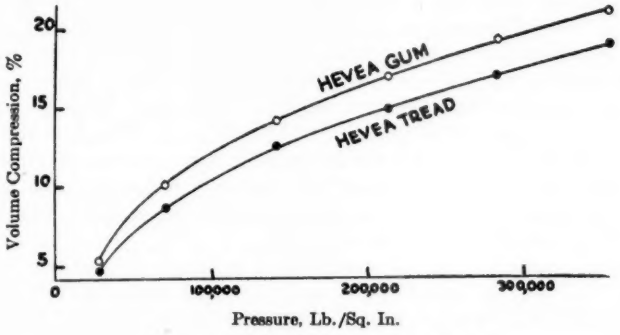

FIG. 1.—Compressibility of cured stocks[3].

Several studies have been made of the effect of pressure on the crystallization of unvulcanized rubber. Thiessen and Kirsch[5] found that pressures in the range from about 150 to 400 pounds per square inch favored the crystallization of rubber. Using a much higher pressure of 114,000 pounds per square inch, Dow has reported[6] that crystallization at 0° C was inhibited. He attributed this to the high viscosity induced in the rubber by the high pressure.

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Wood, Bekkedahl, and Gibson[7] observed that the temperature of melting of a sample of stark rubber was raised from 36° to 70° C by application of 17,000 pounds per square inch.

Chemical investigations at high pressures have been extensive. Fawcett and Gibson[8] discussed the various ways in which pressure might affect the reaction velocity. In the first place, the velocity may increase because of the increased concentration of the reacting substances as the system is compressed. The velocity is a function of the collision rate between the molecules of the reactants, and in a highly compressed gas or liquid the probability of a collision increases, especially as the space occupied by the molecules becomes comparable to the total volume. The reaction velocity would also be influenced by pressure if the potential energy gained by the system as a result of isothermal compression is available as part of the activation energy of the reaction so that there would be an increase in the concentration of activated molecules.

About fifty organic reactions were studied by these authors, with the following general conclusions. All the reactions which proceeded slowly at atmospheric pressure showed increased velocity at the same temperature under higher pressure. The increase in rate in nearly all cases was five- or tenfold by the application of 44,000 pounds per square inch. Reactions which did not proceed at atmospheric pressure (in the absence of catalysts) did not proceed at pressures up to 44,000 pounds per square inch.

A number of investigations of polymerizations at high pressures have been reported and, in general, increased reaction velocities were observed. This might be expected from the idea, to which, however, there are some exceptions, that reactions which are accompanied by a decrease in volume should be accelerated by pressure.

Conant and Tongberg[9] and Conant and Peterson[10] studied the polymerization of isoprene at pressures up to 176,000 pounds per square inch. These authors estimated that raising the pressure from 29,400 to 176,000 pounds per square inch increased the rate about 100-fold. They observed that acceleration of the reaction was more readily accomplished by raising the temperature than by increasing the pressure, but pointed out that there may be cases where the product differs according to whether it is formed at high pressures or elevated temperatures. This would be the case, if there are side reactions with a large temperature coefficient and a negligible pressure coefficient. They also make the interesting conjecture that under high pressure the molecules of the monomer tend to approach definite mutual orientations which are very similar to those which exist in the polymer.

As further examples of polymerizations at high pressures may be cited the work of Dintses, Korndorf, and Lachinov[11], Starkweather[12], Tammann and Pape[13], Zelinskiĭ and Vereshchagin[14], and Sapiro, Linstead, and Newitt[15]. The latter authors make the comment that the advantage of high pressure for polymerizations lies in the fact that it may bring about reaction under comparatively mild conditions and thus minimize deleterious effects of high temperature and drastic catalysts.

The effect of pressure on the velocity of chemical reactions from the standpoint of the transition-state theory has been worked out by Evans[16] and Evans and Polanyi[17], who have emphasized the importance of the density of the transition state for determining the effect of pressure on the reaction velocity. Eyring and his coworkers[18] have included the effects of pressure in their general theory of rate processes. For normal bimolecular reactions, *i.e.*, those which occur at a rate approximately equal to that calculated from the rate of collision

between activated molecules—it is expected and experimentally confirmed that there is a relatively small increase of velocity with increasing pressure. For slow reactions, for which the velocity constant may be smaller by larger factors than that expected from the rate of collision, pressure, on the basis of reaction rate theory, may be anticipated to have a relatively large effect in speeding the reaction. For unimolecular reactions, on the other hand, pressure may have little effect or a retarding influence.

No work appears to have been published on the effects of pressure on vulcanization reactions with rubber. This is surprising in view of the natural technical association of vulcanization with pressure. Molding pressures of considerable magnitude are used in forming most vulcanized rubber articles but these pressures are still not high enough to expect much effect on the course of the vulcanization reactions and the rate of curing. This may help to account for the lack of attention to this subject.

HIGH-PRESSURE MOLDING PROCEDURE

The high-pressure mold was designed for use in a platen type of rubber curing press. To obviate difficulty in removing the vulcanized sample from the mold, the usual design of high-pressure chamber[19] involving only one set of pistons and sealing washers was modified to include pistons at each end of a cylinder bored completely through with a 0.5-inch diameter hole. Figure 2

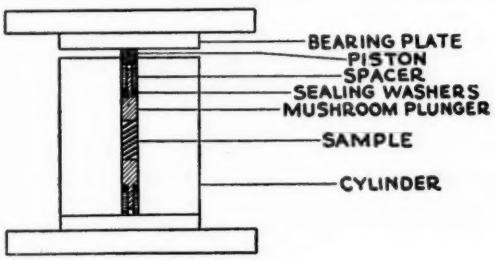

FIG. 2.—High pressure mold.

shows a cross-section of this mold. The length of the mold was 5 inches and the outside diameter 4.5 inches. The principle of the unsupported area is used, the seal being made by means of rubber washers between the mushroom plunger and the spacer. Chrome vanadium steel, S.A.E. 6150, of Rockwell hardness C45 was used for the cylinder. Ball bearing steel, S.A.E. 52100, of Rockwell hardness C65 was used for all pistons and bearing plates. A high-modulus tread stock was found to be most satisfactory for the sealing washers. A special piston 0.5 inch longer than the height of the cylinder was used in an arbor press to eject pistons and sample from the lower end of the mold after curing. Figure 3 is a photograph of the mold and auxiliary parts.

The cures were started with both mold and press platens at room temperature, 77° F. Since, in this procedure, the sample goes through a range of temperatures up to a maximum approximating that of the press platens, it was necessary to determine an equivalent cure time for each length of time the mold was in press. To do this a vulcanized sample containing a thermocouple was placed in the cavity and the lead wires were brought out through a specially

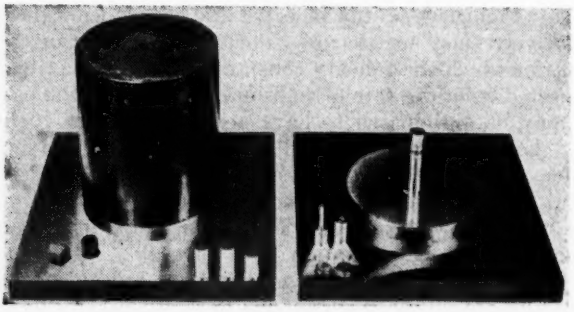

FIG. 3.—High pressure mold.

drilled soft steel piston in one end of the cylinder. Over a period of 2 hours temperature readings of this sample were taken at 5- or 10-minute intervals. At the same time the temperature of the press platens was recorded. A plot of these data is shown in Figure 4. The temperature of the cavity comes to equilibrium at a temperature a few degrees lower than that of the press platens. Using an equivalent cure table for Captax accelerator, based on the principle that an increase of 10° F in vulcanizing temperature causes a decrease by a factor 1.5 in the curing time, the equivalent cure at 275° F for any length of time in the mold was calculated. The equation expressing this relationship is:

$$t_1 = \frac{t_2}{1.5\left(\frac{T_1 - T_2}{10}\right)}$$

where t_1 is time at temperature T_1 equivalent to time t_2 at temperature T_2. These results were plotted as a continuous curve for easy reference.

In curing a sample at high pressure, a weighed amount of stock was placed in the cavity between the plungers, leaving out the small piston at the top of

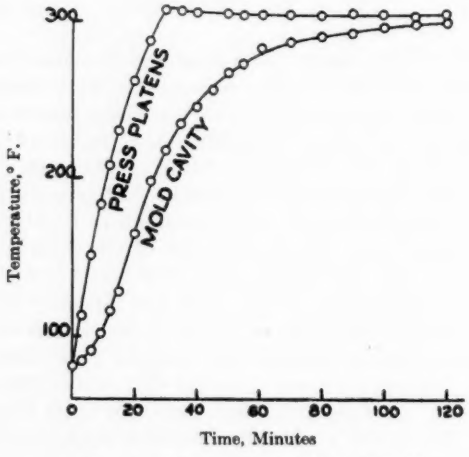

FIG. 4.—Temperature calibration of mold.

the mold. This assembly was then placed between the platens of the press and the heat turned on. The stock was thus heated, without pressure, for 30 minutes, at which time it had reached a temperature of about 220° F. At this temperature the rubber is soft enough to flow but is unvulcanized. Then the press was opened just long enough to insert the small piston in the top of the cylinder. The press was again closed and pumped up to the required pressure. The amount of stock was varied so that, when the desired pressure was attained, the top bearing plate would be within 0.010 inch of the cylinder.

Generally, several samples had to be run for each stock before the exact amount necessary could be determined. Preliminary curing was done with samples 0.5-inch long, but it was soon found that cylinders 1-inch long could be cured as satisfactorily. In all cases the samples were ejected from the mold while hot.

Control samples to compare with those cured at high pressure were vulcanized in a regular type of compression mold having twelve cavities 0.5-inch high by 0.5-inch diameter. The press in the cavities was not determined but can be assumed to conform to standard practice in rubber molding.

The press used for all this work was a Preco hydraulic press having 8-inch square electrically heated and thermostatically controlled platens. The maximum force available from this press was 40,000 pounds. This would permit a maximum pressure in the high pressure mold of about 150,000 pounds per square inch after allowing about 25 per cent loss due to friction. The accuracy of the gage readings appeared to be adequate for this work.

TESTING PROCEDURES

Electrical resistivity and density determinations were made on forty samples of GR-S tread stock for a range of cures and pressures. Density measurements were made by the immersion method in a mixture of water and ethanol, using a chemical balance.

Measurements of electrical resistance were made on an electrometer designed and built by R. B. Stambaugh of Goodyear Research Laboratory. This instrument uses the Westinghouse Type 507 electrometer tube with a Leeds & Northrup potentiometer for null balancing. The samples were prepared by grinding the ends flat and parallel, after which conductive silver paint was applied for electrodes and guard ring.

TABLE I.

COMPOUND FORMULAS USED

Materials	A	B	C	D	E
GR-S	100	100	...	...	...
GR-I	...	...	100	...	...
Smoked sheet	...	...	...	100	100
Sulfur	2.0	2.0	2.0	3.0	3.0
Zinc oxide	5.0	5.0	5.0	3.0	3.0
Softener	3.0	3.0	...	...	...
Stearic acid	2.0	2.0	3.0	4.0	4.0
Captax	1.5	1.5	...	1.0	1.0
Tuads	...	...	1.0	...	...
Anax	1.0	1.0	..	1.0	1.0
Pine tar	...	...	...	3.75	3.75
Carbon black[a]	...	50.0	50.0	...	50.0

[a] Types HPC, EPC, CF, HRF, SRF, Acetylene, P33, and Thermax.

Dynamic tests under compression were made with the Goodyear vibrotester[20] to determine modulus and resilience.

COMPOUNDS USED

The compound formulas used are given in Table I.

Most of the work was done with compound B, GR-S with EPC black, which is referred to in the text and figures as GR-S tread stock.

DENSITY MEASUREMENTS

To produce any permanent change in density of rubber, some sort of realignment of the molecules would have to take place such as occurs in crystallization. In the absence of crystallization, a compressive force would not seem to furnish means for such a change. Substantiation of this view is apparent in the results obtained with GR-S tread stock. On removal from the mold, the samples

TABLE II

DENSITY MEASUREMENTS ON GR-S TREAD STOCK

Vulcanizing pressure (all cures) (lbs. per sq. in.)	Density (g. per cc.)		
	High	Low	Average
1,000	1.1622	1.1579	1.1603
20,000	1.1640	1.1593	1.1618
50,000	1.1625	1.1590	1.1611
100,000	1.1616	1.1600	1.1609

Cure (all pressures) (minutes at 275° F)	Density (g. per cc.)		
	High	Low	Average
25	1.1613	1.1590	1.1600
35	1.1598	1.1593	1.1596
50	1.1625	1.1600	1.1616
70	1.1625	1.1592	1.1612
100	1.1628	1.1579	1.1603
140	1.1625	1.1599	1.1612
200	1.1640	1.1616	1.1626

cured at high pressures expanded sufficiently to return to the density of stocks cured at low pressures. Table II lists the results of these measurements. The average density of all forty samples measured was 1.1611 grams per cc., with an average deviation of ± 0.0011.

ELECTRICAL TESTS

Increases in the pressure of vulcanization caused marked increases in electrical resistivity as may be seen from Figure 5. The electrical resistivity of the GR-S tread stock increased with higher vulcanizing pressures, from 5×10^{13} ohm-cm. for samples vulcanized at 1000 pounds per square inch to 1100×10^{13} ohm-cm. for those vulcanized at 100,000 pounds per square inch. This is interpreted as due to a decrease in flocculation of the carbon black, which in turn is brought about by the very high viscosity of the rubber under pressure. This high viscosity is mentioned by Dow[6] in his crystallization studies. The viscosity of liquids increases at high pressures, so it is probable that the viscosity of rubber becomes very high at 100,000 pounds per square inch. Bridgman[21] discussed the increasing effect of pressure on the viscosity of liquids as the molecular weight and complexity of molecular structure increase. The viscosity of propanol increased 100-fold and pentanol increased 1000-fold under pressure of 155,000 pounds per square inch. Bulgin[22], working with electrically

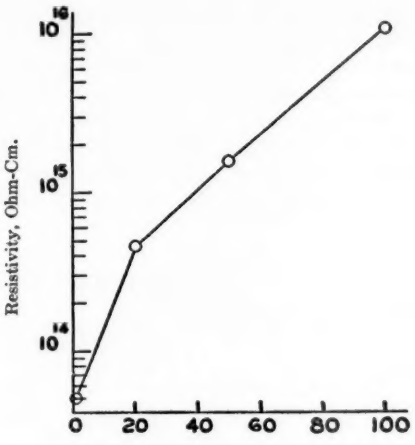

FIG. 5.—Effect of molding pressure on electrical resistance. GR-S tread stock.

conductive rubber, observed an increase in resistivity with increase in molding pressure. This he attributed to the fact that expansion of the rubber after its bulk compression in the mold during cure brought about a separation of the carbon particles. Decreased flocculation of the carbon black may be a more important factor.

DYNAMIC COMPRESSION TESTS

In Figure 6 are plotted dynamic modulus values as functions of pressure and cure for GR-S tread stock. Values for the control samples approach a

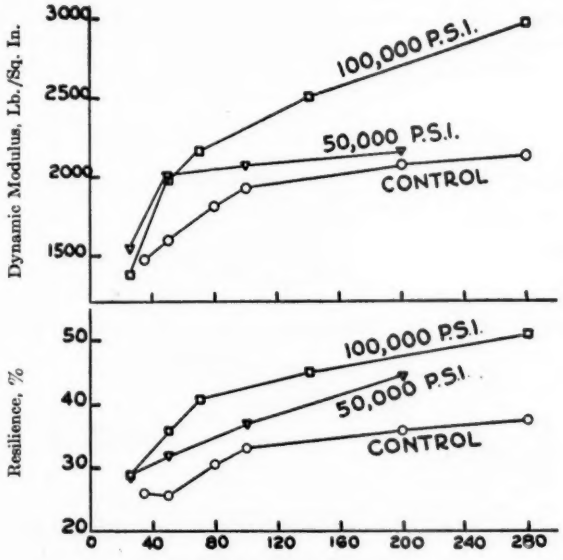

FIG. 6.—GR-S tread stock.

maximum value at 100 minutes of cure, after which a large increase in cure produces only a small increase in modulus. Values for samples cured at 100,000-pound per square inch pressure, however, continue to increase throughout the entire curing range, showing no tendency to level off even at 280 minutes' cure. The 50,000-pound per square inch curve approximates more nearly the control curve than the 100,000-pound per square inch curve, indicating that the pressure effect is one of increasing rate. Figure 6 also shows the resilience values for the same samples. The same order prevails as for the dynamic modulus.

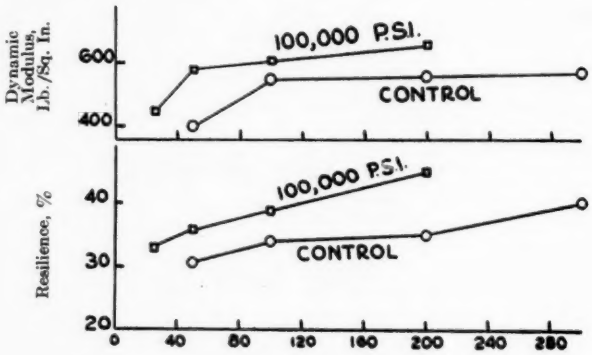

FIG. 7.—GR-S gum stock.

Figure 7 shows curves for GR-S gum stock. Here again the values are greater for samples cured at high pressure, indicating that the effect is not due entirely to carbon black dispersion. Samples sufficiently well cured for testing could be obtained with shorter cures at high pressure than at low pressure.

Figure 8 shows plots of dynamic modulus versus cure for Hevea tread stock. An apparent retardation of cure is reflected here by the considerably lower

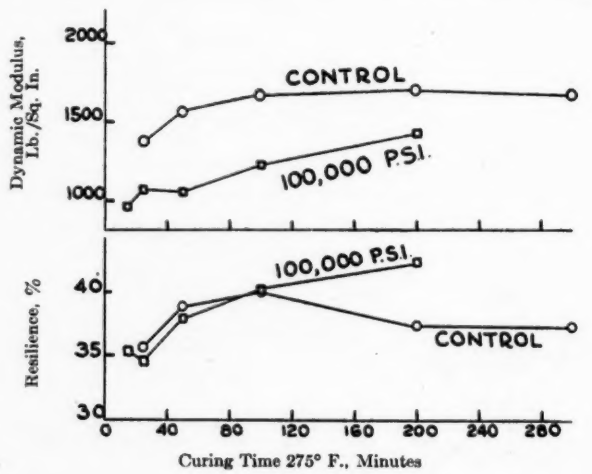

FIG. 8.—Hevea tread stock.

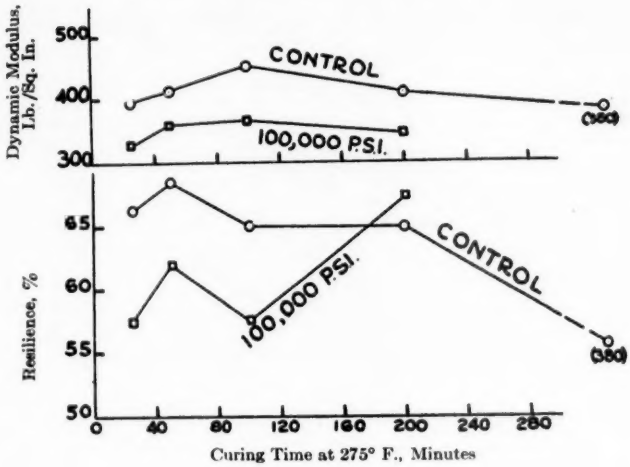

FIG. 9.—Hevea gum stock.

values for the high pressure samples. The resilience, however, also shown in Figure 8, is practically the same for shorter cures and even increases to a higher value for the longer cures. Figure 9 presents the results for Hevea gum stocks, exhibiting the same characteristics as the corresponding tread stock.

Because of the contrasting results obtained with Hevea and GR-S, a series of cures under increasing pressure but constant time and temperature was

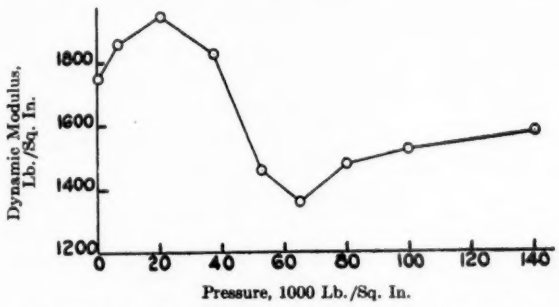

FIG. 10.—Effect of pressure on Hevea tread stock. Cured 100 minutes at 275° F.

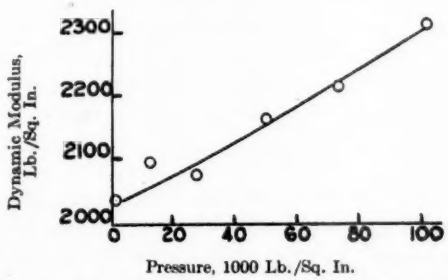

FIG. 11.—Effect of pressure on GR-S tread stock. Cured 100 minutes at 275° F.

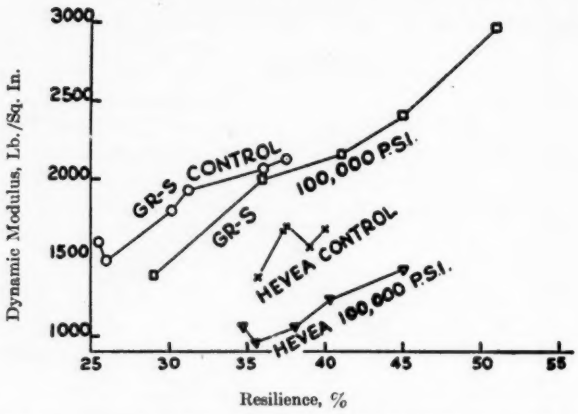

FIG. 12.—Dynamic modulus *vs.* resilience. GR-S and Hevea tread stock.

TABLE III

BUTYL STOCK C VULCANIZED OVER A RANGE OF PRESSURES
(Cured 30 minutes at 307° F)

(Cured 30 minutes at 307° F)

Vulcanizing pressure (lbs. per sq. in.)	Dynamic modulus (lbs. per sq. in.)	Resilience (%)
5,000	1180	12.4
26,000	1010	10.2
38,000	1070	10.3
75,000	1065	11.0
87,000	923	8.6
100,000	945	10.0

TABLE IV

EFFECTS OF DIFFERENT CARBON BLACKS FOR HIGH PRESSURE CURES OF GR-S TREAD STOCK

(Cured 100 minutes at 275° F)

Compound	Black	Diameter of black[a] (mμ)	Per cent increase in dynamic modulus for 100,000 lbs. per sq. in.	Per cent increase in resilience for 100,000 lbs. per sq. in.
B	HPC	24	0	32.1
B	EPC	30	16.35	26.2
B	CF	34	−3.81	16.4
B	HMF	41	26.1	22.2
B	SRF	81	9.4	8.1
B	Acetylene	43	13.8	21.5
B	P33	74	4.95	−1.31
B	Thermax	274	18.5	12.3

[a] Developments and status of carbon black by Isaac Drogin, United Carbon Company, Inc.

undertaken. Hevea and GR-S tread stocks were vulcanized 100 minutes at 275° F under pressures ranging from 500 to 140,000 pounds per square inch. Graphs of dynamic modulus versus molding pressure are shown in Figures 10 and 11. The modulus of the Hevea stock passes through both a maximum and a minimum, though with only slight increase following the minimum.

The modulus of the GR-S stock, however, increases continuously throughout the range investigated.

Figure 12 shows the relation between dynamic modulus and resilience for these tread stocks. For a particular value of modulus, the resilience is always greater for the high-pressure samples than for the low.

A Butyl stock containing HMF black was vulcanized over a range of pressures, holding length of cure and temperature constant. Little change occurs in either modulus or resilience. These values are given in Table III.

Some work was also done to investigate the effects of different carbon blacks for high-pressure cures. Both particle size and type of black seem to have an influence on the results. These results are shown in Table IV. The changes in dynamic modulus and resilience in columns 4 and 5 are for 100,000-pound per square inch vulcanizing pressure, compared to regular curing procedure.

COMBINED SULFUR ANALYSIS

Combined-sulfur determinations were obtained for a limited number of samples. Results of these analyses are plotted in Figure 13. These values substantiate the modulus values obtained with the vibrotester, indicating clearly the reversal of the pressure effect upon Hevea as contrasted to GR-S.

Figure 14 is a graph of combined sulfur as a function of curing time. Curves are shown for GR-S tread stock vulcanized at 1000- and 100,000-pound per

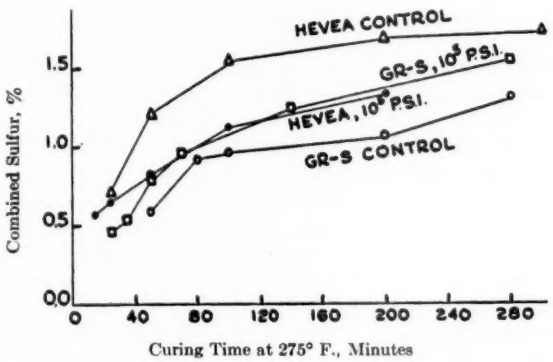

FIG. 13.—Combined sulfur in tread stocks.

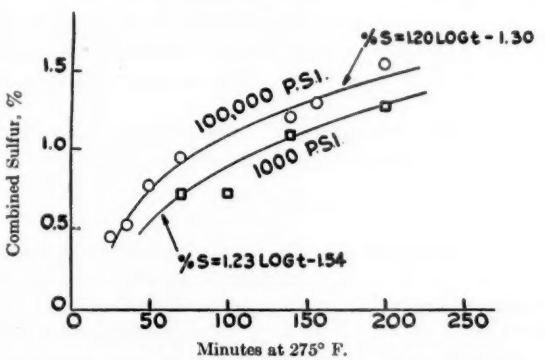

FIG. 14.—Combined sulfur *vs.* length of cure. GR-S tread stock.

square inch pressure. Equations were developed for these two curves and used in determining the pressure coefficient of vulcanization. For the range where the effect of pressure on state of cure is exponential an equation similar to the previously expressed relationship between length of cure and temperature may be applied:

$$t_1 = \frac{t_2}{C^{(P_1 - P_2)}}$$

where t_1 and t_2 are lengths of cure in minutes and P_1 and P_2 are molding pressures in 1000 pounds per square inch.

For this particular GR-S tread stock the value of C, the pressure coefficient of vulcanization, is 1.004. For this stock within the normal curing range increasing the pressure of vulcanization from 1000 to 100,000 pounds per square inch has the same effect on the percentage of combined sulfur as an increase in curing temperature of approximately 10° F.

CONCLUSIONS

One of the most interesting aspects of the results is the contrast in the effects of high-pressure vulcanization on GR-S and Hevea. There is a possibility that the results might be influenced by secondary factors such as differences in the solubilities, melting points, or diffusion rates of the vulcanizing ingredients under high pressure. It seems much more probable, in view of the essential similarity of the two systems, that the contrast in results is related to some difference in the vulcanization reactions with GR-S and Hevea. The apparent retardation of cure by high pressure with Hevea suggests the controlling influence of a reaction with a negative pressure coefficient of velocity, possibly a unimolecular type of reaction. Hauser and Sze[23] have considered that a molecular change in the sulfur from S_8 to S_2 or S_1 is a necessary preliminary of vulcanization. It is difficult to understand why such a reaction should occur differently in Hevea from what it does in GR-S. For a long time there has been a hypothesis that a thermal depolymerization of Hevea takes place during curing which increases its reactivity. Lewis, Squires, and Nutting[24] discount this theory, nevertheless it remains the most attractive explanation of the results obtained here. From this viewpoint, it would be considered that high pressure retards this depolymerization of Hevea to a sufficient extent to make it the controlling reaction for the rate of vulcanization. This is consistent with the improved resilience values secured with Hevea by the use of high vulcanizing pressure.

The concept of two such conflicting reactions during vulcanization has also been formulated by Dogadkin, Karmin, and Golberg[25]. For GR-S, it is then to be assumed that such a depolymerization during cure does not occur to a controlling extent.

A study of the pressure coefficients of vulcanization reactions seems to offer an additional means of investigating these complicated effects.

SUMMARY

A technique was developed for vulcanizing cylinders of rubber 0.5 inch in diameter and up to 1 inch long at pressures as high as 150,000 pounds per square inch, using a small laboratory press (8-inch square platens). The specially designed mold was made of alloy steel according to general principles from the high pressure work of Bridgman[19]. It was prestressed at 200,000

pounds per square inch. The temperature in the mold cavity was carefully calibrated with thermocouples to determine the equivalent length of cure of the test-specimens. Cylinders of GR-S tread stock were vulcanized for a range of cures at 1000, 20,000, 50,000, and 100,000 pounds per square inch. GR-S gum stock and Hevea gum and tread stocks were vulcanized for a range of cures at 100,000 pounds per square inch. Control specimens were cured in a regular type of mold, for which the pressure was not determined. All the volume compression during vulcanization is recovered when the pressure is released. This was determined by precise density measurements of the test-specimens. The electrical resistivity, dynamic modulus, internal friction, and resilience of the test-specimens were determined and the results are discussed.

ACKNOWLEDGMENT

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A METHOD OF MEASURING "HEAT EMBRITTLEMENT" OF GR-S AND HEVEA RUBBER COMPOUNDS *

ALLEN W. SCHOLL AND J. W. LISKA

CHEMICAL AND PHYSICAL LABORATORIES, FIRESTONE TIRE AND RUBBER CO., AKRON, OHIO

This paper is a description of some studies of the phenomenon variously described in the literature as heat embrittlement, heat tenderness, heat shortening, etc. For purposes of discussion the term heat embrittlement will be employed in a general sense to denote the change in breaking elongation resulting from a change in test conditions, *i.e.*, test temperature, cure, or aging. Inasmuch as the expression heat embrittlement is purely qualitative, no definite experimental procedure for its determination is implied, such as is implied, for instance, in the term ultimate tensile strength. Such lack of definiteness in terminology often leads to considerable confusion and the development of widely different test techniques for measuring the same phenomenon. Illustrative of the latter point are two heat embrittlement tests, one introduced by W. B. Wiegand[1] and the other by R. B. Hobson[2]. The first method is based on a measurement of the length of time which a stretched T-50 strip will withstand contact with an iron heated to 400° F without breaking. In the second method, samples of raw polymers are air-aged for specified periods of time, following which benzene solubilities are determined. The amount of residue remaining after extraction is employed as a measure of the heat embrittlement of the material.

With the exception of Hobson's method, there appeared to be general acceptance of the idea that heat embrittlement was correlated in some manner with breaking elongation. It was accordingly decided in this study to measure breaking elongations directly, under various test conditions, and then to express the results in terms of heat embrittlement indices, each of which is defined mathematically. Although these definitions were originally derived on purely empirical bases, they appear to yield results capable of unique and useful interpretations, as will be pointed out later.

TEST APPARATUS

A simple apparatus, shown schematically in Figure 1A and in the photograph Figure 1B, was designed to measure breaking elongations at various temperatures. Ring specimens, S, one inch inside diameter and 1.375 inches outside diameter, died out of 0.075-inch test slabs, were employed throughout. Ring specimens were chosen in preference to the usual dumbbell strip since jaw separation could be used as a direct measurement of elongation, thus eliminating many of the difficulties of measuring bench mark separations on a sample enclosed in a temperature controlled chamber.

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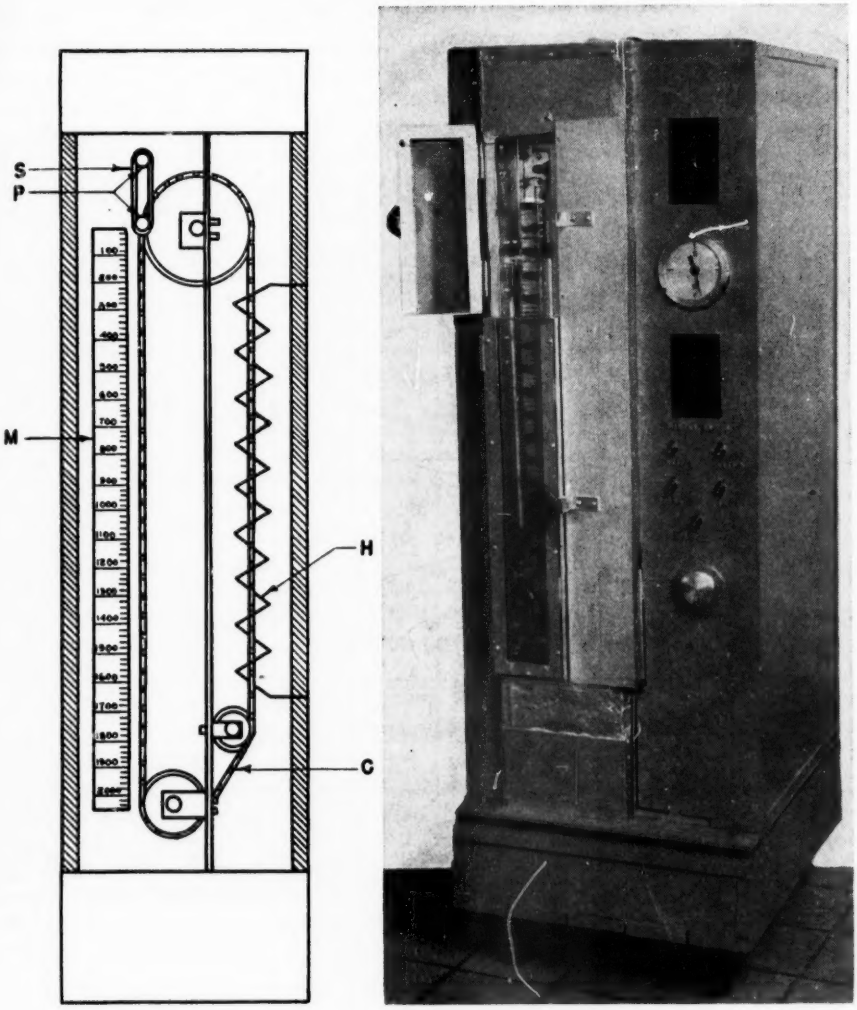

1A. 1B.

FIG. 1A.—Schematic drawing of heat embrittlement apparatus.
FIG. 1B.—Photograph of heat embrittlement test apparatus.

The test unit is essentially an air oven (equipped with automatically controlled heaters H), in which are mounted two stainless steel posts P (0.375 inch in diameter and free to rotate) one fixed and one movable. The movable post is fastened to an endless chain C, which is driven at the rate of 20 inches per minute. Thermostatically controlled air is circulated through the test chamber by means of a blower. To reduce heat losses during loading operations, flap valve (not shown) was installed over the outlet of the blower in such a manner that air circulation was cut off as soon as the loading door was opened. Closing of the door lowered the flap valve, thus allowing free circulation of air during the preheating and actual testing operations.

GENERAL TEST METHOD AND CALCULATIONS

Preliminary tests (made by inserting fine wire thermocouples in the center of the test-piece) indicated that the ring samples employed reached the test temperatures in 60 to 70 seconds after being placed in the test chamber. As an added precaution, a preheating time of 90 seconds was finally adopted as standard, since this also provided a reasonable time schedule for loading the preheated sample on the posts, elongating it to break, noting the elongation on the scale M, declutching the motor drive, and returning the movable post manually to its original position.

For most of the tests described, standard test temperatures of 100 and 200° F were employed.

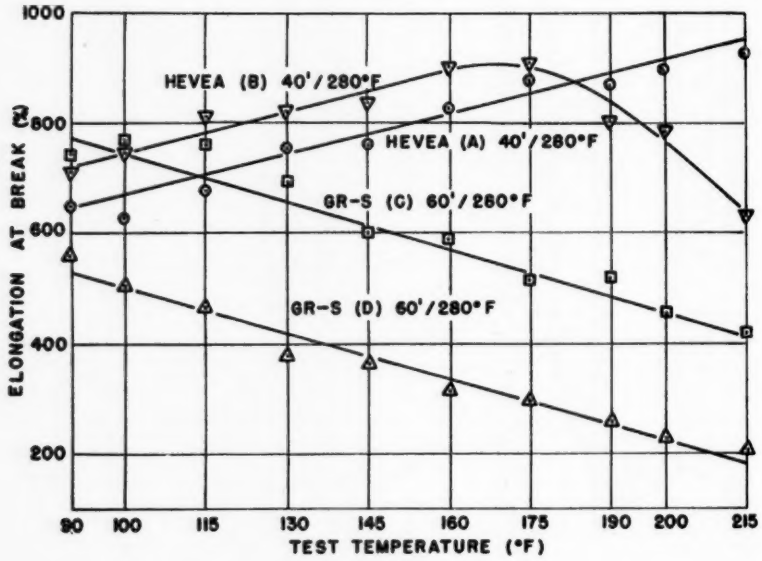

FIG. 2.—Effect of test temperature on breaking elongation.

Now the difference between the breaking elongations at these two temperatures is certainly a measure of heat embrittlement. It is, however, equally certain that this difference is not adequate in itself, since a very "short" compound might have a small difference, and thus would be considered to have good heat embrittlement characteristics. Specification of the magnitude of the breaking elongations at, say, 100° F plus the difference in the breaking elongations at 100 and 200° F would aid in interpreting the data correctly, but this method has the obvious disadvantage of yielding a dual number quality index. Reduction of the data to a percentage basis, *i.e.*, division of the difference in breaking elongations by the breaking elongation at 100° F, was also found to be inadequate, since it did not sufficiently compensate for "short" stocks. Hence to attain the desired objective, a single index which would (at least in the majority of cases tested) give sufficient weight to the magnitude of the breaking elongation, the following empirical definition of the normal heat

embrittlement index F_H was evolved:

$$F_H = \frac{E_{100} - E_{200}}{(E_{100})^2} \times 10^4 \quad (1)$$

where E_{100} is the breaking elongation at 100° F, and E_{200} is the breaking elongation at 200° F.

The factor 10^4 was introduced simply as a means of obtaining whole numbers rather than decimals for use as indices.

Although this definition is admittedly empirical, it does have mathematical implications: namely, that the percentage decrease in breaking elongation and the reciprocal of the breaking elongation at 100° F are of equal weight or importance in determining the magnitude of the heat embrittlement index. One further advantage appears on examination of *Hevea* rubber and GR-S compounds by this method. In the former instance (for normal or slightly aged samples) negative values of F_H are obtained, since E_{200} is greater than E_{100}.

Typical data, showing the relation between test temperature and breaking elongation of two GR-S and two *Hevea* compounds are shown in Figure 2. Calculation of the heat embrittlement factors of these compounds yields negative values for the *Hevea* compounds and positive values for the GR-S compounds. *Hevea* compound A was loaded with 41 parts HPC black; whereas B contained 48 parts zinc oxide and 3.2 parts HPC black per 100 parts of polymer. The GR-S compounds C and D were loaded with 40 parts HPC black and a mixture of 13 parts HPC and 14 parts SRF black, respectively, per 100 parts of polymer. The cures employed were commercial optimum cures in all cases.

DISCUSSION OF RESULTS

The effect of cure on the heat embrittlement factor, F_H.—The normal heat embrittlement factors, F_H, of two GR-S and two *Hevea* compounds are shown in Figure 3. The heat embrittlement factors for the *Hevea* compounds, although negative, increased with increased time of cure and remained negative even for the 100 per cent overcures. The *Hevea* compound containing high zinc oxide is seen to have larger F_H values than the carbon black compound for the commercial optimum cures. The heat embrittlement factors for the GR-S compounds also increased with increased time or cure, although they were positive throughout the curing range studied.

The effect of air aging on the heat embrittlement factors F_H of tread-type compounds.—Normal heat embrittlement factors, F_H, were obtained on *Hevea* (E) and GR-S (F) tread-type compounds (each loaded with 45 parts HPC black per 100 parts of polymer), which had been air-oven aged at 212° F for various periods of time up to 72 hours.

The data, shown in Figure 4, illustrate the fact that F_H increases with time of aging for both *Hevea* and GR-S compounds, although for the early part of the aging period F_H is negative for the *Hevea* compound.

The data also indicate the possibility that on further air aging, the *Hevea* compound might be poorer than the GR-S compound from the standpoint of heat embrittlement. This possibility is probably not important from a prac tical viewpoint, however, since in both cases the physical properties are very low after 72 hours of air aging at 212° F.

The effect of accelerators on the heat embrittlement factor F_H.—Six experimental GR-S compounds cured with Santocure, Monex, Altax-DPG, Altax,

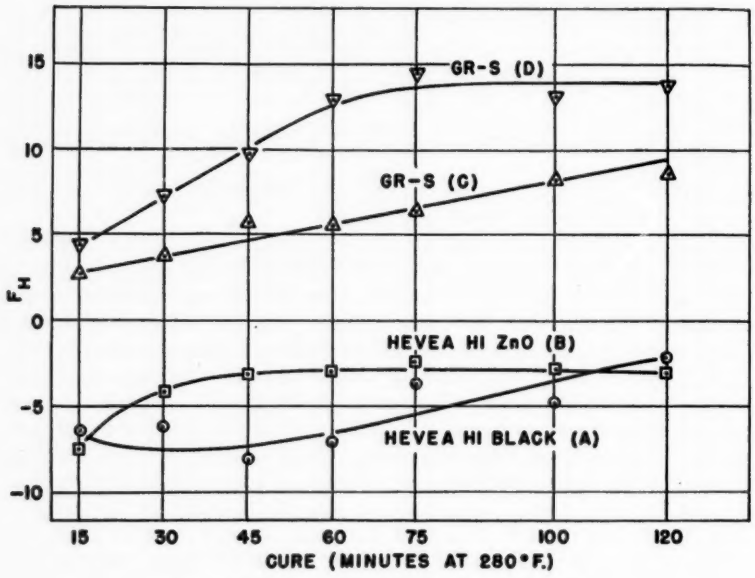

FIG. 3.—Effect of cure on heat embrittlement factor F_H.

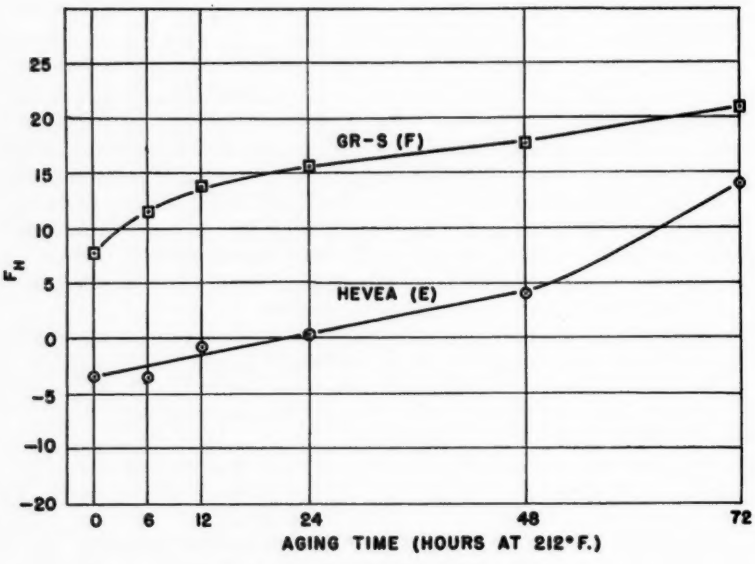

FIG. 4.—Effect of air oven aging on F_H.

Erie-Safex, and Captax-litharge accelerators were tested by the technique described. The compounds used were typical GR-S mixes containing 45 parts EPC black per 100 parts polymer. The results of the heat embrittlement tests are shown in Table 1.

TABLE 1

EFFECT OF ACCELERATORS ON F_H

Stock Curing time (min. at 280° F)	G Santocure	H Monex	I Altax-DPG	J Altax	K Erie-Safex	L Captax-litharge
	Calculated heat embrittlement factors, F_H					
20	—	—	—	—	—	3.6
30	4.2	5.1	6.6	—	—	4.3
35	—	—	—	—	—	—
40	—	5.3	—	—	—	6.0
45	5.8	—	—	—	5.3	—
50	—	5.9*	5.8	—	—	5.5*
60	6.8*	—	—	7.3	7.6	—
65	—	5.8	6.0*	—	—	6.4
75	7.8	—	—	—	6.4*	—
80	—	5.8	—	5.4	—	7.0
85	—	—	6.1	—*	—	—
100	8.1	5.5	—	6.4	6.5	—
110	—	—	6.8	—	—	—
120	8.2	—	—	—	—	—
125	—	—	—	—	7.4	—
130	—	—	7.8	6.6	—	—
150	—	—	—	—	6.7	—
160	—	—	—	8.0	—	—
200	—	—	—	8.0	—	—

* Commercial optimum cure.

The data indicate that at optimum cure for each of the compounds tested the effect of the various accelerators on F_H was small; the Captax-litharge combination was slightly the best, and Santocure the worst. The effect of overcure on F_H, however, was found to be small in the case of the Monex compound. Compounds containing each of the other accelerators tested were found to have F_H values which increased appreciably with time of cure.

The effect of antioxidants on the heat embrittlement factors F_H of GR-S compounds.—A large batch of antioxidant-free GR-S latex was prepared and then divided into several portions. To each portion one of the materials listed below was added as a stabilizer before coagulation. The antioxidants used were:

2% AgeRite Powder
2% Neozone-A
2% Santoflex-B
2% B-L-E
2% Stalite
2% Santoflex-BX
2% Flectol-H
2% AgeRite Resin
2% V-G-B
2% Stabilite

The base recipe used in compounding is given in Table 2. Test slabs were cured 60 minutes at 280° F. The ring specimens were prepared and tested, as previously described, and the heat embrittlement factors F_H were then calculated. The corresponding heat embrittlement factors F_H are given in Table 3.

TABLE 2

BASE RECIPE—ANTIOXIDANT SERIES

Ingredient	Amount
GR-S	100.0
Santocure	1.7
Sulfur	2.0
Zinc oxide	3.3
HPC black	40.0
Paraflux	4.5
Bardol	4.6
Pine tar	1.0
Total	157.1

TABLE 3

HEAT EMBRITTLEMENT FACTORS—ANTIOXIDANT SERIES

Feature	F_H
AgeRite Powder	3.3
Neozone-A	5.2
Santoflex-B	3.7
B-L-E	3.5
Stalite	4.3
Santoflex-BX	4.6
Flectol-H	4.2
AgeRite Resin	4.2
V-G-B	4.1
Stabilite	4.8

TABLE 4

BASE RECIPE—SULFUR SERIES

GR-S	100.0
Zinc oxide	2.4
Sulfur	Variable
Stearic acid	2.5
AgeRite Powder	0.6
Pine tar	2.6
Bardol	4.0
EPC black	45.0
Santocure	1.2

TABLE 5

HEAT EMBRITTLEMENT FACTORS OF SULFUR SERIES COMPOUNDS

Parts sulfur (min. cure at 280° F)	1.0	1.5	2.0	2.5	3.0	3.5
	Heat embrittlement factor					
30	4.6	4.8	4.2	4.4	6.0	5.6
50	4.4	5.4	6.1	6.6	9.0	9.5
75	4.7	6.5	8.1	8.6	11.5	11.8
100	5.1	7.0	8.5	10.0	11.7	14.5
125	5.7	7.1	9.1	10.3	13.1	13.3
150	5.5	6.7	10.2	11.0	12.4	13.0

The Neozone A-GR-S compound was found to give the largest heat embrittlement factor and therefore would be judged the most undesirable of those tested.

The effect of sulfur content on the heat embrittlement factor F_H of GR-S compound.—Six GR-S compounds were prepared with various proportions of sulfur (1.0 to 3.5 parts in increments of 0.5-part), according to the formula shown in Table 4.

An increase in sulfur was found to increase the heat embrittlement factors over the range of cures investigated. The compounding features and the corresponding heat embrittlement factors are given in Table 5.

It is interesting to note that the above results agree with those of Vila[3], who also concluded that high sulfur led to "short" or brittle compounds.

GENERAL CONCLUSIONS AND DISCUSSION

The methodological definition of a heat embrittlement factor evolved in this work appears to yield results which are consistent with experience, indicating a fundamental difference between *Hevea* and GR-S compounds and providing a single index value for comparison purposes.

The apparatus described is simple and can readily be reproduced.

Consideration of the definition of F_H and some of the factors which affect elastomer quality suggests rather interesting variations in the methods described. It is possible, for instance, to define heat embrittlement factors other than the one described earlier in the report by the name, normal heat embrittlement factor F_H. A factor F_H', defined by the expression:

$$F_H' = \frac{E_N - E_A}{E_N^2} \times 10^4 \tag{2}$$

where E_N = elongation at break of normal stock, and E_A = elongation at break of aged stock, would yield information regarding the effect of aging on heat embrittlement.

Similarly:

$$F_H'' = \frac{E_N - E_{OC}}{E_N^2} \times 10^4 \tag{3}$$

where E_N = elongation at break of normal stock, and E_{OC} = elongation at break of overcured stock, would yield indices showing the effects of cure on heat embrittlement.

Although no study has been made as yet of the properties of F_H' and F_H'', it is possible, of course, that they would be of more interest than F_H. Further work along this line is required to clarify this point.

ACKNOWLEDGMENT

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PROPERTIES OF EBONITE. XXXVII. ELECTRICAL PROPERTIES OF SYNTHETIC RUBBER EBONITES *

D. G. FISHER, L. MULLINS, AND J. R. SCOTT

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS,
48 TEWIN ROAD, CROYDON, ENGLAND

INTRODUCTION

A previous investigation by the Research Association of British Rubber Manufacturers[1] showed that the German Buna synthetic rubbers can produce ebonites superior in some respects to ebonite from natural rubber, notably in their smaller deformation at elevated temperatures and, excepting Buna-N, lower dielectric power loss at radio frequencies. Like natural-rubber ebonite, however, they suffer from deterioration of electrical surface resistivity when exposed to light[2].

The heat resistance of ebonites made from butadiene polymers and from butadiene-styrene and butadiene-acrylonitrile copolymers has been noted in other investigations[3] although no data showing such superiority have been published[4]. Good electrical properties have been found at least for butadiene-styrene copolymers[5]. Generally, however, such systematic investigations as have been made on ebonites from synthetic rubbers, such as those from GR-S[6] and Hycar OR-15[7], did not include electrical properties. Accordingly it was decided to study synthetic rubber ebonites, with special reference to electrical properties, as part of the Joint Ebonite Research of the Electrical Research Association and the Research Association of British Rubber Manufacturers.

EXPERIMENTAL DETAILS

SYNTHETIC RUBBERS EXAMINED

These are listed in Table 1; all were of American manufacture except the Buna-85 (German, prewar sample) and Thiokol-AZ (British).

TABLE 1

Synthetic rubber	Prepared from
Buna-85	Butadiene
GR-S, type CC[d]	Butadiene 75%, styrene 25%
Hycar-EP	Butadiene 60%, styrene 40%
Perbunan (Stanco)	Butadiene 70%, acrylonitrile 30%
Hycar OR-15	Butadiene 60%, acrylonitrile 40%
Thiokol-RD	Butadiene plus a nitrogen compound[a]
Neoprene-GN	2-Chlorobutadiene
Neoprene-I	2-Chlorobutadiene plus an unsaturated nitrile[b]
Thiokol-AZ	Ethylene tetrasulfide[c]
Thiokol-FA	Polysulfide[c] prepared from dichlorodiethyl ether

[a] Nitrogen content of Thiokol-RD 3.9%.
[b] Neoprene-I contains 32–33% chlorine and 2.5–3% nitrogen.
[c] This is the basic unit of the polymer, although not used as such in making the polymer.
[d] This type of GR-S gives the following average analytical figures: acetone extract 6.3%, fat acid 4.4%, soap 0.8%, ash 1.2%, heat loss 0.2%.

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MIXES AND VULCANIZING CONDITIONS

Mixes A–G were composed of rubber (natural or synthetic) 68, sulfur 32, diphenylguanidine 2: A, natural rubber (smoked sheet); B, GR-S; C, Hycar-EP; D, Perbunan; E, Hycar OR-15; F, Thiokol-RD; G, Buna-85.

These were press-vulcanized for 4 hours at 153° C. Although 2 hours is adequate for natural rubber in such a mix[8], the longer period was chosen because previous work suggests that synthetic rubbers generally vulcanize more slowly[9].

TABLE 2

Mix	H	J	K	L	M	N
Neoprene-GN	88	88	88	—	—	—
Neoprene-I	—	—	—	88	—	—
Thiokol-FA	—	—	—	—	68	—
Thiokol-AZ	—	—	—	—	—	68
Natural rubber	—	—	—	—	5	5
Sulfur	32	32	32	32	32	32
Magnesium oxide	3.5	3.5	3.5	3.5	—	—
Zinc oxide	—	10	10	—	10	10
Butyraldehyde-aniline	1.6	1.6	—	1.6	—	—
Diphenylguanidine	—	—	—	—	2	2
Vulcanization (hrs. at 153° C)	8½	8½	8½	8½	—	—

Mixes H to N had the compositions shown in Table 2. The Neoprene mixes were based on those from reference 13.

The small amount of natural rubber in mixes M and N was included, following the usual practice with Thiokol, to facilitate the mixing process.

TEST METHODS

Measurements of permittivity and power factor were made on standard specimen of 22 cm. diameter and 3 mm. thick, with tinfoil electrodes of 15 cm. diameter[10]. Audiofrequency tests (0.8 and 1.6 kc. per sec.) were made on a Schering bridge; in the radiofrequency band (119 to 2,500 kc. per sec.) the method was substitution in a circuit adjusted to resonance, a resistance and a capacitance in series being substituted for the sample.

Two series of tests were made: (1) at room temperature (about 20° C), at frequencies of 0.8, 1.6, 119, 278, 500, 902, 1,030, 2,060, and 2,500 kc. per sec. (mixes A to E only); (2) at 1,000 kc. per sec. at temperature intervals of 10° C in the range 20° to 120° C.

DISCUSSION OF RESULTS

THIOKOLS AND NEOPRENES

The Thiokol mixes M and N failed to give a hard product when vulcanized at 153° C; indeed the stocks became extremely soft and finally almost liquid. Statements in the literature about the production of ebonitelike materials from thioplasts are contradictory. It has been stated[11] that Thiokols A and F and Perdurens G and H cannot be made into ebonite. On the other hand, products resembling hard rubber are said to be obtainable from Thiokols, either the ordinary types[12] or a special molding powder[13], and there is a reference[14] to "mixes of the ebonite type" made from the closely similar material Ethanite; products from Thiokol molding powder are claimed to have "advan-

tageous electrical properties (*i.e.*, lower power factor, dielectric constant, and dielectric strength) equal to the electrical properties of the best rubber[15]." Even more definite are statements[16] that ebonite from "thiocaoutchouc" (presumably a thioplast) differs little in dielectric properties from high-grade natural-rubber ebonite, except that the loss angle (power factor) is much higher and the resistivity lower; unfortunately none of the accessible references quotes mix formulas or other data. As the production of ebonites from the thioplasts evidently involves the development of special types of mix, and the technical value of the products seems open to doubt, this subject was not pursued further.

The Neoprene mixes H and L containing butyraldehyde-aniline gave hard products, but with so high a dielectric loss that this type of mix was not considered to merit further study. Mix K, containing zinc oxide gave an ebonite, even when the butyraldehyde-aniline was omitted; this may be because Neoprene-GN contains a thiuram disulfide[17], a type of compound which accelerates the vulcanization of ebonite[8]. In both J and K, the presence of zinc oxide caused the surface to be extremely hygroscopic, so that in course of time drops of a strongly acid aqueous liquid formed on the surface; for this reason no tests were made on these ebonites. This hygroscopicity is due to zinc chloride formed during vulcanization, and might therefore have been avoided by using litharge in place of zinc oxide, as has been recommended for a natural-rubber ebonite mix containing Neoprene[18]. However, in view of the poor dielectric properties of mixes H and L, Neoprene seemed unlikely to give a satisfactory electrical ebonite. This is in keeping with the fact that soft Neoprene vulcanizates have high permittivities (6 to 7) and power factors (9 to 12 per cent)[19]. It has been stated[20] that flexible ebonite made from a mixture of natural rubber and Neoprene has "good electrical properties", but no data are given, and as the article referred to deals only with the use of such ebonite in electroplating equipment, the statement doubtless implies merely that the volume resistivity is reasonably high.

NATURAL RUBBER AND BUTADIENE-TYPE SYNTHETIC RUBBERS

Permittivity and power factor are plotted against temperature and frequency in Figures 1–4; in Figures 1 and 3 the frequency increases from right to left to show more clearly the relation between temperature and frequency

FIG. 1.

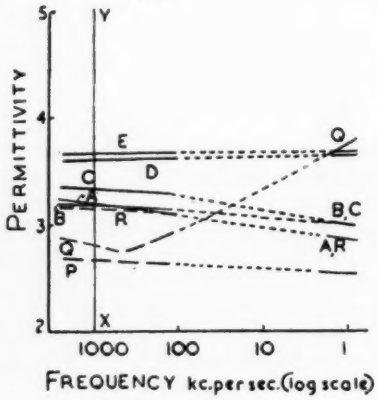


FIG. 2.

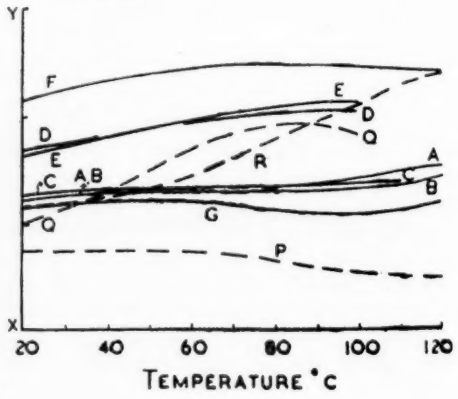


FIG. 3.

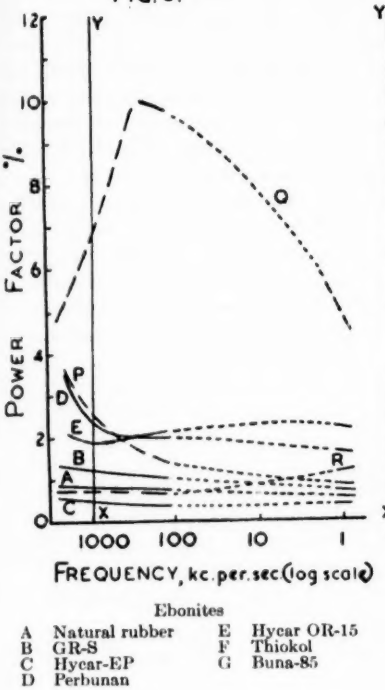
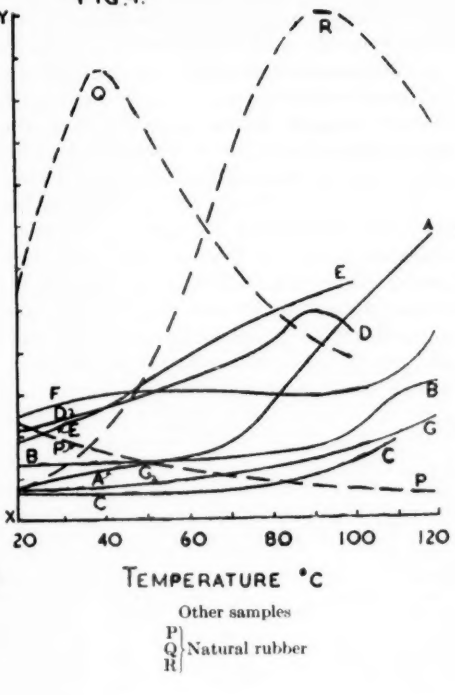


FIG. 4.



Ebonites

A	Natural rubber	E	Hycar OR-15
B	GR-S	F	Thiokol
C	Hycar-EP	G	Buna-85
D	Perbunan		

Other samples

P, Q, R } Natural rubber

effects (see the section on Effects of Frequency and Temperature). The figures include data for the following additional samples, which are used in discussing this relation:

Mix	P	Q	R
Natural rubber	100	90	80
Sulfur	2	10	20
Zinc oxide	5	—	—
Stearic acid	2	—	—
Benzthiazoyl disulfide	1.5	—	—
Diphenylguanidine	—	2	2
Vulcanization °C	153	141	141
min.	30	180	180

Comparison of types of rubber.—As the main object of the Joint Ebonite Research was the study of dielectrics for radio and other high-frequency applications, the loss factor (permittivity × power factor) at 1,000 kc. per sec. was selected as the best index to the utility of the ebonites. These values are shown in the left-hand section of Table 3; the right-hand section gives earlier data for ebonites from the same rubbers or from German synthetic rubbers of similar composition.

Judged by the data in Table 3, copolymers of butadiene and styrene containing 35–50 per cent of styrene (Hycar-EP and Buna-SS) are the best of the rubbers examined for radio-frequency applications, although an earlier (1943) sample of Hycar-EP gave a very poor result—loss factor about 0.07—so the question of variability requires attention.

All the polymers containing polar groups (Hycar OR-15, the Perbunans, Perbunan Extra, and Thiokol-RD) give such high loss factors that they must be considered unsuitable for high-grade electrical ebonites.

The three intermediate rubbers (Buna-85, natural rubber, and GR-S) fall in different orders of merit in the various series of tests; in particular, the choice between natural rubber and GR-S depends on whether normal or elevated temperatures have to be considered (temperature effects are discussed more fully in the section on the Effects of Frequency and Temperature).

The data of Gartner[21] in Table 3 indicate that in the series Buna-85–Buna-S–Buna-SS the loss factor at 0.05 kc. per sec. decreases progressively as butadiene is replaced by styrene; this is not seen at 1,000 kc. per sec., since Buna-S and GR-S both show a higher loss than Buna-85 (or -115). However, such comparisons are not reliable, because the power loss must be influenced by the variable amount and nature of the polar substances present as emulsifiers, coagulants, antioxidants, and so on.

TABLE 3

LOSS FACTOR OF EBONITES

Frequency (kc. per sec.)	1,000		0.050	1,000	
Temperature (° C)	20	90	(a)	20(b)	
Hycar-EP	0.017	0.032	0.009	—	Buna-SS
Buna-85	0.021	0.043	0.0225	0.013(0.015)	Buna-85 (115)
Natural rubber	0.0295	0.134	0.016	—	Natural rubber
GR-S	0.0405	0.053	0.0155	0.0235	Buna-S
Hycar OR-15	0.068	0.213	0.0395	—	Perbunan Extra (I.G.)
Perbunan (Stanco)	0.076	0.198	0.0415	—	Perbunan Extra (I.G.)
Thiokol-RD	0.102	0.128	—	—	—

(a) Room temperature; each figure shown is the mean for two ebonites with different proportions of sulfur (data of Gartner[21]).
(b) Each figure is the mean for two ebonites vulcanized for different periods (data of Scott[22]).

A particularly interesting comparison would be that between Buna-S and GR-S; the higher loss factor for the latter, compared with Buna-S at 20° C and 1,000 kc. per sec., can be ascribed partly to the use of diphenylguanidine as accelerator in the GR-S ebonite, but the observed difference (0.017) is greater than the effect of this accelerator in Buna-85, according to Table 3 (increase in loss factor = 0.008), or its previously observed effect in natural-rubber ebonite (increase in loss factor less than 0.006, according to Fisher, Newton, and Scott[8]).

Effects of frequency and temperature.—Theoretical considerations[23] indicate that raising the temperature should produce qualitatively similar effects to reducing the frequency, for which reason the frequency scale in Figures 1 and 3 has been reversed.

Permittivity of the ebonites changes very little with frequency over the two ranges examined (see Figure 1); although no data were obtained between 1.6 and 119 kc. per sec., it is unlikely that the permittivity here deviates much from the values found in these two frequency ranges. Changes in power factor (Figure 3), though larger, are still relatively small except with Perbunan (mix D) at the highest frequencies. Usually the power factor tends to be greater the higher the frequency. Hycar-EP (C) retains its superiority over natural rubber (A), and the latter its superiority over GR-S (B), throughout the frequency range, but the differences between these three ebonites are greater at the higher frequencies.

The usual effect of raising the temperature is to increase permittivity, but the effect is never large and there are consequently no marked differences in temperature-sensitivity from one ebonite to another (Figure 2).

The changes of power factor with temperature (Figure 4) are the most important effect observed. Again the general tendency, within the temperature range examined, is an increase, though sometimes there are signs of a maximum and an eventual decrease (this is clearly shown by the vulcanizates Q and R made with less sulfur). The course of the change in power factor with temperature divides the ebonites into three groups:

(1) Natural-rubber ebonite (A) shows a rapid increase beginning between 60° and 70° C.

(2) Ebonites B, C, F, and G, made from the butadiene polymer (Buna-85), butadiene-styrene copolymers (GR-S and Hycar-EP), and Thiokol-RD, show little change up to about 90° C; consequently the GR-S ebonite (B), although inferior to the natural-rubber ebonite (A) at room temperature, is superior at temperatures above about 50° C, while Hycar-EP (C) and Buna-85 (G) become increasingly better than natural rubber as the temperature is raised.

(3) Ebonites D and E made from the butadiene-acrylonitrile copolymers (Perbunan and Hycar OR-15) show a more or less continuous increase, except for an apparent maximum with the former.

TABLE 4

INTERSECTION POINTS OF POWER FACTOR CURVES

Intersection	(1) Power factor on temperature graph	(2) Power factor on frequency graph	(3)* dt	(4)* df	(5)* dt/df
D and E	2.5	2.1	16° C	0.7	23° C
B and R	1.2	0.9	8	1.6	5
P and R	1.7	1.0	16	2.3	7
D and R	2.9	1.45†	28	3.65	7.5
Q and R	6.8	?2†	45	?5	?9

* See text below.
† By extrapolation.

The vertical line XY on each of Figures 1 to 4 represents the same test conditions, namely 20° C and 1,000 kc. per sec.; hence if rising temperature and decreasing frequency were exactly equivalent, the course of the curves to the right of these lines should be similar on the temperature and frequency graphs.

The permittivity curves are mostly too flat to afford a good test of the correctness of this expectation, but some confirmation is provided by mix Q, which shows the most steeply rising curves in both Figures 1 and 2.

With power factor, although complete similarity between the frequency and temperature curves is not observed, there is a general resemblance in that the curves for mix P fall continuously, Q passes through a maximum, R rises, D and E intersect to the right of the line XY, and A and B gradually converge (and finally intersect on the temperature graph). The essential difference between Figures 3 and 4 is that in passing from left to right the temperature curves lie progressively higher than the corresponding frequency curves. This is illustrated by considering the points of intersection of the curves; these occur at the power factor values shown in columns 1 and 2 of Table 4, and are always higher on the temperature graph than on the frequency graph.

It thus appears that increasing temperature, besides producing effects analogous to those of decreasing frequency, causes a progressive increase in power factor. This may be ascribed to ionic conduction, which increases rapidly and progressively with temperature. The existence of this effect explains why the curves for the ebonites rise on the temperature graph but generally fall on the frequency graph.

It is interesting to consider the distances of these intersection points to the right of XY; these are shown in Table 4 as dt (distance on temperature graph) and df (distance on $\log_{10}$ frequency scale). On the hypothesis that rising temperature and decreasing frequency are equivalent, the ratio dt/df would represent the temperature difference corresponding to a ten-fold change of frequency. Although no great accuracy can be claimed for the values of this equivalence factor, especially in view of the complications introduced by ionic conduction, it is interesting to note that they are mostly within the range of values (5°–9° C) found by Aleksandrov and Lazurkin[24] from a study of the effects of temperature and frequency on mechanical deformations of soft rubber.

SUMMARY

Experiments were carried out to explore the possibility of making good electrical ebonites from various types of synthetic rubber. The ebonites produced were tested for permittivity and power factor over wide ranges of temperature and frequency.

Thioplasts (Thiokols AZ and FA) apparently do not produce hard ebonite-like vulcanizates by the normal procedure. Neoprenes (GN and I) give ebonites, but with such high dielectric power loss as to be unsuitable for use as high-frequency dielectrics; moreover, if the mix contains zinc oxide, the ebonite has a very hygroscopic and therefore electrically unsatisfactory surface.

Butadiene copolymers containing polar groups (butadiene-acrylonitrile types and Thiokol RD) give ebonites with high power loss, hence are not suitable for making high-grade electrical ebonites.

Polybutadiene (Buna-85) and butadiene-styrene copolymers (GR-S, Hycar-EP, Buna-S) are much nearer to natural rubber as far as the radio-frequency (100 to 2,500 kc. per sec.) power loss of their ebonites is concerned. The GR-S ebonite examined was not so good as natural rubber at room temperature, but was superior above about 50° C. Buna-85 and Hycar-EP were superior to natural rubber over the whole temperature range; indeed, the high-styrene copolymers, as represented by Hycar-EP and Buna-SS, appear to be the best type of synthetic rubber for making ebonite with low power loss, especially at high frequencies and temperatures.

The effects of changing temperature and frequency on permittivity and power factor are discussed. Attention is drawn to the big effect of temperature on power factor; this was less with polybutadiene and butadiene-styrene ebonites than with natural rubber ebonite, in keeping with the greater heat resistance of the former as judged by plastic yield tests.

Comparison of the effects of rising temperature and decreasing frequency shows that these produce broadly similar effects on power factor, as would be expected on theoretical grounds, but that rising temperature superposes a second effect (an increase), presumably due to increased ionic conduction.

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THE STRUCTURE OF NEOPRENE. II. DETERMINATION OF END GROUPS BY MEANS OF RADIOSULFUR *

W. E. MOCHEL AND J. H. PETERSON

CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO., WILMINGTON, DELAWARE

It is now generally agreed that in the free radical polymerization of vinyl compounds and dienes, fragments of the initiator become combined as end groups in the polymer molecules[1]. The polymerization catalysts, so-called, are compounds that decompose under polymerization conditions to form free radicals, which in turn become the true primary initiators. In some cases it has been postulated, on the basis of kinetics studies, that the catalyst first combines with the monomer to produce a complex which subsequently rearranges to an activated molecule[2], but the structure of the resulting polymer would also involve the catalyst or some fragment as a terminal group. However, not all polymer molecules need have the primary initiator as an end group. For example, it has recently been demonstrated[3] that the thiols used as regulators, or modifiers, particularly in diene polymerizations, are chain transfer agents[4] which likewise become attached as end groups on the polymer molecules. Other possibilities must also be considered, such as chain transfer with monomer and termination of two chains by mutual interaction without combination[5] to yield additional types of end groups.

Determination of the end groups in Neoprene (polychloroprene) was therefore undertaken to obtain further knowledge about the structure and formation of this synthetic elastomer. The general purpose chloroprene polymer, Neoprene Type GN, is prepared in aqueous emulsion by a free radical mechanism initiated with potassium persulfate; the polymerization is carried out in the presence of elemental sulfur, and the final latex is treated with tetraethylthiuram disulfide. Thus the product may contain sulfur from any of three different sources. For a study of this type[6], radiosulfur, S^{35}, was particularly convenient because it could be used to label the different sulfur-containing materials added[7].

RESULTS AND DISCUSSION

Sulfur modification.—In the polymerization of Neoprene Type GN, elemental sulfur dissolved in the monomer appears to act as a polymerization modifier. Without the sulfur, an insoluble, nonplastic polymer is formed even at low conversion, but polymerization of chloroprene containing 0.5–1.5 per cent of sulfur to approximately 90 per cent conversion followed by treatment with 2.5 per cent of tetraethylthiuram disulfide yields a soluble, plastic polychloroprene. To investigate the mechanism of this sulfur modification, radiosulfur was used to tag the modifier in a typical Neoprene Type GN emulsion polymerization system[8] and polymer samples, after extraction with acetone to remove free sulfur, were analyzed for combined modifier sulfur by radioactivity assay.

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TABLE I

RADIOSULFUR-TAGGED MODIFIER IN NEOPRENE TYPE GN

Conversion (%)	Tagged sulfur content (%)			
	Original		Thiuram-treated	
4	0.299	0.303	0.189	0.189
15	.223	.223	.196	.201
27	.250	.309	.201	.201
36	.278	.269	.224	.216
45	.282	.278	.255	.243
54	.296	.299	.264	.273
62	.333	.321	.276	.283
69	.355	.344	.279	.275
75	.396	.400	.325	.314
86	.383	.385	.234	.232

As indicated in Table I, the sulfur modifier content, after extraction of the uncombined sulfur, generally increased with conversion both in the original samples, *i.e.*, before treatment with tetraethylthiuram disulfide, and after the thiuram treatment. This gradual increase in sulfur modifier content was probably due to the increasing sulfur/monomer ratio as polymerization progressed, rather than to any significant change in mechanism. About 30–60 per cent of the 0.7 per cent of tagged sulfur added to the monomer became combined, but part of that originally combined appeared to be lost during the thiuram disulfide treatment. Statistical analysis of the data for combined modifier sulfur indicated a probability of less than 1 per cent that the differences between untreated and thiuram-treated samples were due to experimental error. Reëxtraction of the samples with acetone for three days failed to change the sulfur contents significantly and this procedure appeared satisfactory for removal of free sulfur[9].

The thiuram disulfide treatment appeared to remove some radiosulfur, but this was shown to be due to an exchange reaction which as yet has not been completely elucidated. The ratio of tagged sulfur, by radioassay, to total sulfur, as determined by chemical analysis, was lower for untreated polymers (average 1.4) than for those treated with tetraethylthiuram disulfide (average 1.8). Also, the total sulfur content remained relatively constant while the radiosulfur content decreased as the amount of tetraethylthiuram disulfide added was increased (see Table II).

TABLE II

EFFECT OF TREATMENT ON TAGGED SULFUR CONTENT

Polymer treatment before coagulation, stabilized with	Sulfur (%)		Ratio
	Tagged	Total	
Phenyl-α-naphthylamine	0.37	0.51	1.4
1% Thiuram disulfide	0.27	0.47	1.8
2.5% Thiuram disulfide	0.24	0.47	2.0
5% Thiuram disulfide	0.21[a]	0.48	2.3

[a] Standard deviation was only 0.004%.

Sulfur extracted from a thiuram-treated polymer was recrystallized from acetone (m.p. determined was 119.5–120°; original sulfur, m.p. 119–120° and mixed m.p. 118–119°) and found to have a specific activity of 2490 counts per milligram per sixty-four seconds, compared to the specific activity of 5025 for the original sulfur. Although sulfur and tetraethylthiuram disulfide refluxed

in boiling acetone or benzene did not appear to exchange appreciably in two hours, a radio exchange did occur when sulfur and the thiuram were heated together in a melt at 95–100° as shown in Table III.

Recrystallized thiuram recovered from one of these melts was shown by analysis to be radioactive. On the basis of reported thiuram chemistry[10] it is probable that the sulfur and thiuram disulfide react under these conditions to form a thiuram polysulfide in which sulfur exchange occurs and that this polysulfide decomposes again to the disulfide and free sulfur. The recovery of sulfur or thiuram disulfide was never quantitative; there was always a non-crystallizable oil left.

Although it was demonstrated that sulfur exchange with tetraethylthiuram disulfide can occur in a melt at 95–100°, the conditions used for the Neoprene treatment were considerably different, and the same mechanism may not hold. The polychloroprene latex (pH 11.5–12.0) was treated with a dispersion of the thiuram at 40° for a few minutes, the latex coagulated and, after drying two or three days at room temperature under vacuum, the polymer was extracted with boiling acetone for three days. Furthermore, the indicated exchange in Neoprene must involve combined sulfur, not elemental sulfur alone (see Table I), although the sulfur involved may be bound only by coördinate linkages to other sulfur atoms.

TABLE III

SULFUR-TETRAETHYLTHIURAM DISULFIDE EXCHANGE
(Initial S:S* ratio was 2:1)*

Sulfur	Specific activity counts/64 sec./mg.
Original	2609
After 30 min. at 95–100°	2416
Original	2100
After 7 hr. at 95–100°	710
Original	2144
After 16 hr. at 95–100°	744

* S* is used to indicate radioactive tagged sulfur.

Further evidence that there is a reaction between the combined sulfur modifier and the tetraethylthiuram disulfide was obtained from changes in properties of the polymer. The sulfur-modified polymers prepared in 10 to 90 per cent conversion were insoluble in benzene or chloroform and nonplastic if isolated from the latex without treatment with tetraethylthiuram disulfide but, after treatment in alkaline emulsion, corresponding polymers were completely soluble and plastic. This solubilization of gel polychloroprene did not occur appreciably unless the sulfur modifier was used. At monomer conversions below 10 per cent, sol polymer of very high intrinsic viscosity was isolated without thiuram treatment but the intrinsic viscosity was decreased by treatment with the thiuram disulfide.

A polychloroprene made in 80 per cent conversion with 0.7 per cent of radioactive tagged sulfur and treated with 2.5 per cent of tetraethylthiuram disulfide was extracted with acetone to remove uncombined sulfur and fractionated from benzene solution using methanol as precipitant[11]. The results of analyses of the fractions, shown in Table IV, indicate an approximate constancy of combined sulfur from the modifier over a range of molecular weights from 92,000 to 321,000.

Obviously the sulfur was not acting as an "end grouper" like the typical chain transfer agents, since some thirty-one sulfur atoms were combined in

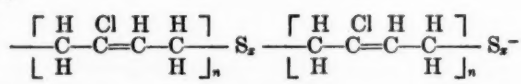
TABLE IV

FRACTIONATED NEOPRENE TYPE GN CONTAINING RADIO-SULFUR

Fraction	Weight (g.)	$\bar{M}n$[b]	S* (%)	S* atoms/mol.	$\bar{M}$/S* atom	Total sulfur (%)
A	2.97	Gel[a]	0.38			
B	6.35	321,000	.31	31.0	10,300	0.59
C	6.79	210,000	.30	20.2	10,400	.37
D	4.85	132,000	.31	12.8	10,300	.36
E	3.18	92,000	.34	9.8	9,400	.40
F	3.03	63,200	.38	7.5	8,400	.46
G	3.54	40,000	.46	5.7	7,000	.75

[a] Fraction gelled during preparation for molecular weight measurements.
[b] Number average molecular weight by osmotic pressure measurement.

each polymer molecule, on the average, in fraction B. On the basis of this evidence the sulfur is believed to be combined essentially as a comonomer, as has been demonstrated in the case of oxygen[12]. This hypothesis is also in accordance with the observation by Schulz[13] that sulfur is a polymerization inhibitor for styrene, *i.e.*, sulfur reacts with the free radicals to form new, inactive, resonance-stabilized radicals. However, in the case of chloroprene the free radicals ending in sulfur can continue growth. Contrary to the situation in the reaction of oxygen with styrene, the addition of sulfur to the chloroprene free radical appears to be much slower than the growth reaction; consequently, only a small amount of sulfur becomes combined and high molecular weight copolymers are obtained. The number of sulfur atoms combined successively has not been determined but it is probably of the order[14] of 2–6. From the chloroprene to sulfur ratio it may be postulated that the structure of Neoprene Type GN before treatment with tetraethylthiuram disulfide is, in part, the following, where x may be 2 to 6 and n is, on the average, 80 to 110 times x (the observed values are higher because of the sulfur exchange)



(Nonlinear linkages of an unknown nature are undoubtedly also present in minor amounts.) The sulfur linkage is believed to be cleaved by a reaction with tetraethylthiuram disulfide, or its alkaline degradation products, by a mechanism still under investigation. This cleavage yields a soluble, plastic polymer by reducing the average molecular weight below the critical value for gelation[15]. Thus sulfur, unlike thiol modifiers, does not directly control molecular weight but yields a product whose molecular weight can subsequently be reduced by the necessary amount to render the gel soluble.

Persulfate initiation.—To investigate the mechanism of polymerization initiation by persulfates, polychloroprene was prepared using as catalyst, or initiator, potassium persulfate tagged with radiosulfur. The removal of all uncombined persulfate fragments from the polymers was the greatest difficulty in this work. For example, a typical polymer (prepared in 70 per cent conversion with 0.6 per cent of potassium persulfate), differed in its persulfate sulfur content when treated in various ways as shown in Table V.

After examination of several possibilities, three successive precipitations of the polymers from dilute benzene solution with acetone appeared to be the best procedure for removal of uncombined residues; the tagged sulfur content

could thus be reduced to about 0.004–0.005 per cent, with a standard deviation of 0.0006 per cent. The possibility must always be considered that the samples assayed contained residual uncombined inorganic residues from the persulfate. Since rather lengthy treatment of the samples was necessary to obtain constant reproducible analytical values, it may be possible that some persulfate sulfur originally combined was lost by hydrolysis or ester interchange, but this is unlikely at the temperatures involved[16].

Within experimental error there appeared to be no significant differences in amount of combined persulfate sulfur at different monomer conversion levels.

Fractionation of differently modified polychloroprenes initiated with tagged persulfate, by precipitation from benzene solution with methanol, yielded high molecular-weight fractions having relatively high tagged sulfur contents and low molecular-weight fractions having little or no combined persulfate sulfur. Results obtained for an unmodified polymer, one modified with 0.7 per cent of elementary sulfur and one modified with 0.30 per cent of dodecanethiol, indicated a difference in the mechanism of initiation (see Table VI). Since these fractionations were carried out in identical manner, it is believed that comparison of the results gives a valid indication of a difference in mechanisms.

TABLE V

POLYCHLOROPRENE MADE WITH RADIOPERSULFATE

Successive treatments	Time	Tagged sulfur (%)
None (original polymer)	...	0.102
Mill-washed with 60° water	20 min.	0.056
Mill-wash repeated	30 min.	.054
Extracted with acetone	3 days	.049
Extracted with methanol	3 days	.036
Original extracted with boiling water	3 days	.040
Dissolved in benzene and precipitated with methanol	...	.0091

The unmodified and sulfur-modified polychloroprenes contained combined sulfur from the persulfate, indicating actual chain initiation by a persulfate fragment[17], probably SO_4^-. In the case of the sulfur-modified, thiuram-treated polymer, Neoprene Type GN, the radiosulfur assay indicated that from 8 to 17 polymer molecules were formed per combined sulfur atom from the primary initiator and reaction kinetic chain lengths ranged from approximately 1,000,000 to 5,000,000. The formation of 8 to 17 polymer molecules for each primary initiator, presumably by chain transfer with monomer, is not at all unlikely and is of the same order of magnitude as has been reported for other systems[18].

The unmodified polymer, isolated at very low monomer conversion to obtain a soluble product, contained less persulfate sulfur than the Neoprene Type GN but the amount combined was significantly more than in the case of the thiol-modified polymer. Reaction kinetic chain lengths for the unmodified polymer ranged from 5,000,000 to 8,000,000, running through 10 to 52 polymer molecules, for each persulfate sulfur atom combined. Of course, the kinetic chain lengths would be lower if monomer initiation occurred with other free radicals such as hydroxyl, formed by reaction of persulfate with water. Hydroxyl free radical combination is a possibility which has not been excluded[19].

TABLE VI

FRACTIONATED POLYCHLOROPRENES MADE WITH TAGGED PERSULFATE

Fraction	Weight (g.)	Mol. wt.[a]	Tagged sulfur (%)	S*/mole/g.	Mols./S* atom[b]
Unmodified Polymer (5% Monomer Conversion)					
Whole	35.5	.....	0.005		
A	8.37	.....	.0074		
B	14.72	.....	.0017		
C	4.20	1,810,000	.0014	25.3	
D	1.90	.....	.0009	...	
E	1.92	525,000	.0006	3.15	10
F	1.35	318,000	.0004	1.27	25
G	1.22	205,000	.0004	0.82	39
H	0.57	124,000	.0005	.62	52
I	.26	.....	.0007	...	
Sulfur-Modified Polymer (83% Monomer Conversion)					
Whole	26.2		0.073		
C	6.72	410,000	.0007	2.87	11
D	3.03	218,000	.0015	3.27	10
E	2.16	150,000	.0026	3.90	8
F	1.02	111,000	.0033	3.66	9
G	0.73	85,000	.0028	2.38	13
H	.98	74,000	.0025	1.85	17
Dodecyl Mercaptan-Modified Polymer (69% Monomer Conversion)					
Whole	33.0		0.048[c]		
B	6.30	610,000	.059	360	
C	6.62	365,000	.0004	1.48	22
D	5.53	264,000	.0003	0.80	40
E	1.50	208,000	Nil	...	..
F	3.00	140,000	Nil[d]	(0.085	377)

[a] Molecular weights were determined viscometrically and checked osmotically.
[b] Calculated number of polymer molecules per tagged-sulfur atom.
[c] Reprecipitation three times from benzene reduced tagged sulfur content to 0.005%.
[d] Analysis of a large sample at a long counting period indicated the presence of 0.00006% of tagged sulfur.

In the case of the thiol-modified polymer the final fractions of the polymer contained practically no persulfate sulfur. The amount of persulfate sulfur remaining in fraction F would correspond to a kinetic chain length of approximately 53,000,000, running through 377 molecules, which is considered too high. Chain transfer should not change the reaction kinetic chain length[20] but only the average degree of polymerization. On the basis of available evidence it is proposed that a different initiation mechanism is operating in the presence of the dodecanethiol. It is believed that the potassium persulfate reacts with the dodecanethiol to form free radicals which in turn initiate the polymerization. A possible reaction is:

$$K_2S_2O_8 + 2RSH \rightarrow 2RS + 2KHSO_4$$

It may be this type of reaction which is responsible for the promoter action of thiols, particularly in butadiene polymerization[21].

Since the high molecular weight fractions always contained large amounts of radiosulfur, the possibility must be considered that molecules initiated by persulfate fragments precipitated with the high molecular-weight polymer because of reduced solubility. (It is highly improbable that the persulfate-initiated polymer molecules would, on the average, grow to longer polymer chain lengths than others.) It is believed that residual uncombined persulfate

fragments, *i.e.*, inorganic sulfates having low solubility in benzene, are carried down by the high molecular-weight fractions as they precipitate. The potassium acid sulfate expected would have low solubility in benzene and might need only the nucleus of precipitating polymer to be carried down.

Thiol modification.—To complete this investigation it was considered desirable to examine the action of dodecanethiol, a typical chain transfer agent[3], in the polymerization of chloroprene. Accordingly, radiosulfur-tagged dodecanethiol was substituted for the sulfur modifier in a typical polymerization system for Neoprene Type GN and the polymer obtained was analyzed, after extraction with acetone.

TABLE VII

THIOL-MODIFIED NEOPRENE (0.30% $C_{12}H_{25}SH$)

Conversion (%)	Mol. wt.[a]	S*	S* atoms/mol.
10	148,000	0.025	1.15
20	175,000	.025	1.36
30	165,000	.025	1.28
41	207,000 (?)	.026	1.68
50	192,000	.019	1.14
59	232,000	.021	1.52
69	161,000	.025	1.26
86	Contained gel	.026	...
		Average	1.34

[a] M_n by osmotic pressure.

Typical results, illustrated in Table VII, indicated that the polymers isolated at 10–86 per cent conversions contained on the average more than one thiol sulfur atom per polymer molecule. Complete precipitation of these polymers from benzene solutions failed to change the sulfur contents appreciably, and a duplicate experiment gave similar values for sulfur content; therefore it is believed that the sulfur remaining was actually combined in the polymer molecules. Note also that there was no significant change in sulfur content as the conversion changed, indicating uniform thiol consumption. About 50 per cent of the added thiol was combined.

TABLE VIII

FRACTIONATED NEOPRENE MODIFIED WITH 0.30% TAGGED THIOL (69% CONVERSION)

Fraction	Mol. wt.[a]	S* (%)	S* atoms/mol.	$\frac{\%S^*}{100} - \frac{32}{\overline{M}}$
Whole	256,000	0.019	1.52	6.5×10^{-5}
A	1,150,000	.010	3.58	7.2
B	890,000	.011	3.05	7.4
C	610,000	.011	2.09	5.7
D	415,000	.013	1.68	5.3
E	312,000	,013	1.26	2.7
F	250,000	.016	1.25	3.2
G	198,000	.019	1.17	2.8
H	165,000	.026	1.34	6.5
I	119,000	.032	1.19	5.0
J	82,000	.013 (?)	0.33 (?)	
K	75,000	.049	1.14	6.2
			Average	5.3×10^{-5}

[a] $\overline{M}_n$ by osmotic pressure.

TABLE IX

FRACTIONATED NEOPRENE MODIFIED WITH 1.0% RADIOTHIOL (45% CONVERSION)

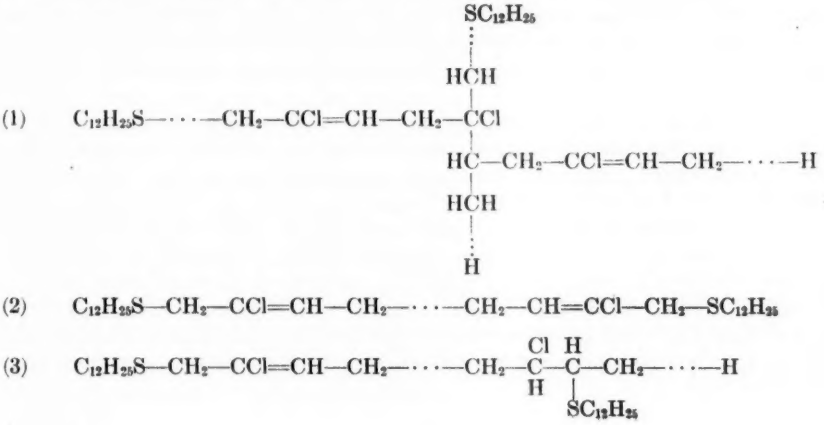
Fraction	Mol. wt.[a]	S* (%)	S* atoms/mol.	$\frac{\%S^*}{100} - \frac{32}{\bar{M}}$
Whole	58,000	0.072	1.30	17×10^{-5}
B	160,000	.035	1.75	15
C	130,000	.043	1.74	18
D	103,000	.047	1.51	16
E	74,000	.054	1.25	11
F	59,000	.075	1.38	14
G	40,000	.104	1.30	24
			Average	16×10^{-5}

[a] Viscometrically; C and D checked by osmotic pressure, which indicated $\bar{M}_n$ = 126,000 and 103,000, respectively. Whole polymer by osmotic pressure.

Fractionation of the dodecanethiol-modified polymer likewise indicated an average of slightly more than one thiol sulfur atom combined per polymer molecule, even after extensive reëxtractions and reprecipitations (see Table VIII).

A polymer was prepared using 1 per cent of dodecanethiol tagged with radioactive sulfur and was fractionated after three complete precipitations to remove uncombined thiol residues. This polymer, of lower molecular weight, and presumably containing fewer side branches per molecule, contained an even greater excess of combined thiol sulfur over the theoretical one atom per molecule than the fractions of corresponding molecular weight from the low thiol polymer (see Table IX). Similar results were obtained with a product isolated at 25 per cent conversion to reduce the branching still further.

From these results it was apparent that the dodecanethiol was not combined in a simple 1:1 ratio of thiol to polymer molecule, as would be expected for linear polymer if only chain transfer were involved[22]. There are three obvious ways in which the thiol content could be increased: (1) cross-linking reactions involving growth through double bonds in the polymer chains[23], (2) mutual combination of two growing chains initiated by RS to give a maximum of two sulfur atoms per molecule; (3) addition of thiol molecules to the double bonds in the polymer chains by the usual free radical mechanism[24]. These reactions would give rise to the structures:



Mechanism 1 undoubtedly is operative and probably accounts at least in part for the higher-than-average sulfur content of fractions A and B. However, since 1.0 per cent thiol yielded polymers containing more sulfur than those made with only 0.30 per cent of the thiol it appears that mechanisms 2 and/or 3 are important. Increased amounts of thiol might well lead to a larger number of growing chains at any given moment and hence a higher probability of termination by mutual combination (mechanism 2); but this mechanism alone cannot lead to the values 3.58 and 3.05 found for fractions A and B of Table VIII. In view of the mild conditions employed for free-radical addition of thiols to double bonds of butadiene polymers and rubber[25], mechanism 3 appears to be the most probable as an explanation of the results observed. The last columns of Tables VIII and IX express the amount of combined sulfur in excess of the theoretical one atom per polymer molecule, reduced to a common molecular weight. The values indicate that, on the average, the second atom of sulfur becomes combined after reaction kinetic chain lengths of 600,000 and 200,000, respectively, for polymerization in the presence of 0.30 and 1.0 per cent of dodecanethiol. The average value for the reduced excess sulfur content for the 1 per cent thiol polymers is approximately three times the value obtained when roughly a third as much thiol was used. This is strong evidence for a simple mass effect which would be more likely in mechanism 3 than in the others.

EXPERIMENTAL DETAILS

Materials.—The radiosulfur used in this investigation was supplied as irradiated potassium chloride by Clinton Laboratories (now Oak Ridge National Laboratory) and was obtained on allocation from the U. S. Atomic Energy Commission. Carrier sulfur was added and the labeled sulfur isolated by a series of operations involving oxidation to sulfate, precipitation as barium sulfate, reduction to barium sulfide, conversion to hydrogen sulfide and oxidation to free sulfur[26]. It was recrystallized from carbon disulfide before use. This sulfur had an original activity of 1.3×10^6 counts per mg. per 64 seconds.

To prepare potassium persulfate the stock solution of tracer as potassium sulfate plus potassium chloride was converted to potassium hydrogen sulfate and oxidized electrolytically to potassium persulfate[27], containing radiosulfur.

For the preparation of dodecanethiol containing radiosulfur, the radioactive barium sulfide described above was acidified and the hydrogen sulfide was passed into a methanol solution of sodium methoxide to form sodium hydrosulfide. This was then treated with dodecyl bromide at 120° in a pressure tube for three hours and the radiosulfur-labeled dodecanethiol was isolated and distilled (104–110° (3 mm.)) to yield a product of 96 per cent purity by iodometric titration.

Polymerization.—The polymerizations were carried out in the usual manner[28] at 40°. The sulfur-modified polymers were made with 0.7 per cent sulfur. The thiol-modified polymers were prepared in the same way, substituting 0.30–1.0 per cent of dodecanethiol for the sulfur. Likewise, for the unmodified polymer no change in the system was made except omission of the modifier. Samples of the latex were removed, treated with 2.5 per cent of tetraethylthiuram disulfide in emulsion or with 0.5 per cent of phenothiazine and 1.0 per cent of phenyl-α-naphthylamine in emulsion. They were then coagulated with ethanol and dried at room temperature *in vacuo*. Analysis indicated that polymers prepared in this way contained only small amounts of residual soap and other adjuvants.

Preparation of samples.—As indicated in the Discussion, the polymer samples were extracted or precipitated to remove uncombined sulfur and sulfur compounds. For elemental sulfur and some thiol samples the polymers were extracted continuously with acetone or methanol for three to four days in ASTM rubber extractors or Soxhlet apparatus. In other experiments the samples were dissolved in benzene to make 1–5 per cent solutions and the polymer precipitated completely by addition of about 2 volumes of methanol or acetone. Further addition of methanol produced no cloudiness in the clear supernatant liquid.

Radioactivity assay.—The dry polymer samples were oxidized by the Carius method to obtain a clear solution of sodium sulfate. The sulfate was precipitated as the benzidine salt on special funnels, dried and counted directly with Geiger counters[29]. A control from the labeled sulfur compound under study was always counted at the same time as the unknowns to eliminate the necessity of reliance on decay calculations and to check counter operation with theory based on decay. Sufficient sodium sulfate carrier was added to both control and unknowns to make the sample sizes comparable so that errors due to absorption were eliminated. Furthermore, the control samples were adjusted to roughly the same order of magnitude of counts as the unknowns.

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SUMMARY

By use of radioactive sulfur it has been shown that sulfur-modified Neoprene, *i.e.*, Neoprene Type GN, is essentially a copolymer of chloroprene and sulfur in the approximate ratio of 100 chloroprene units per sulfur atom. The sulfur units, possibly disulfides, are cleaved by an alkaline emulsion of tetraethylthiuram disulfide, so that a gel polymer containing combined sulfur can thus be converted to a soluble, plastic product. The mechanism of this cleavage reaction has not been completely elucidated as yet.

Potassium persulfate, used as initiator for the polymerization of Neoprene, appears to be combined with the polymer in Neoprene Type GN in amounts equivalent to 8–17 polymer molecules formed for each sulfur-containing initiator fragment. However, when dodecanethiol is used as modifier, a large proportion of the polymer molecules contain essentially no combined sulfur from the persulfate, and it appears that the true initiator is the RS free radical formed by reaction of the thiol with potassium persulfate.

Dodecanethiol used as a polymerization modifier or chain transfer agent is combined in a greater amount than the one thiol per polymer molecule expected on the basis of simple chain transfer. High molecular-weight fractions contained 3–4 thiol sulfur atoms per polymer molecule and the results suggest that thiol addition to the double bonds of the polymer had occurred.

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PHOTOELASTIC APPLICATIONS IN RUBBER TECHNOLOGY*

JAMES A. HURRY AND DOUGLAS CHALMERS

GATES RUBBER CO., DENVER, COLORADO

We believe this paper will be of interest both to rubber product design engineers and to rubber product compounders. Both groups were represented in its preparation. To the rubber product engineer it suggests a brief, practical, quantitative method for determining the probability that his design will withstand the forces to which the product will be subjected in service. To the compounder who has frequently wondered how certain formula specifications are derived, it represents a much needed step preceding laboratory and service testing to insure that stock requirements are realistically established.

PHOTOELASTIC ANALYSIS AND PRODUCT DESIGN

Photoelastic analysis holds particular promise in rubber product design. The technique for suitable low modulus model material is described and qualitative applications on sections of models of rubber molded products and test-specimens are illustrated. The technique is applied to a typical processing problem encountered in the rubber industry. A brief extension of the method to quantitative analysis is presented with reference to the physical and photoelastic constants of the material used. The effect of the nonlinear stress-strain condition is included.

THE GENERAL PROBLEM OF PRODUCT DESIGN

Product design, expressed simply, is the distribution and profiling of selected structural materials so that they will best withstand service requirements. These requirements may be related to simple tension, compression, and shear stresses. They may be more complex, as encountered in torsion and bending, which are made up of combinations of tension, compression, and shear.

The force reactions which products must undergo may be further complicated by time and frequency factors. High force magnitudes in short times of application represent shock or impact problems. More moderate forces applied over a long-time period introduce creep or flow phenomena. These represent permanent deformation because of the plastic phase found to some degree in all materials. Forces may be applied in cycles over a wide range of frequencies. Such cyclic forces may be in directions causing flexing in tension, compression, shear, torsion, simple bending, and combinations of these.

Structural materials of substantially rigid nature have been found to obey such predictable relations as Hooke's Law over a measurable range of their ultimate strength in any direction. This simply says that any force (stress) produces a proportional deformation (strain).

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A measurable physical relation like this, coupled with the tools of mathematics such as graphical analysis, analytical geometry, trigonometry, and the calculus, make reasonably practical the drawing board design of rigid materials into immediately successful products and structures. Many phases of mechanical, civil, and electrical engineering lend themselves to such a high degree of technical control of design.

It is also a frequently encountered principle of dynamic design that maximum life is associated with cyclic stresses at the lowest possible percentage of rupture stress. This is the so-called stress-minima criterion of optimum design for longest dynamic life. Effective design, therefore, entails not only selecting materials of known ultimate strength, but a knowledge of the ratio of actual service stress to ultimate strength.

DESIGN LIMITATIONS IN RUBBER TECHNOLOGY

The rubber product design engineer too frequently finds that the generalized equations of the basic engineering sciences do not adequately cover the conditions and variables encountered in his problem. Rubberlike materials show nonlinear relation of stress and strain. This nonlinear relation would be no great design problem if it were constant or even practicably controllable. Generalized expressions could then define it. Unfortunately the nonlinear condition is not only greatly affected by material composition and method of preparation, but also by time and temperature of testing or service. Rubberlike materials further display considerably higher degrees of strain per unit stress than are encountered with usual engineering materials. Those relations the rubber product designer does find and measure are therefore generally complicated beyond the practical use of conventional mathematics of even the highest order insofar as using them to predict service behavior is concerned. We do not mean by this statement to belittle the skillful application of engineering mathematics to certain products and phases of product design of long standing in the rubber industry. These limitations apply particularly to the preliminary layout of new products, to new conditions for old products, or to an analysis of some new aspect in performance encountered in an old product.

THE ROLE OF PHOTOELASTIC ANALYSIS

The design method to be described is not a substitute for drawing board design or for the principles of mechanical engineering. It represents a valuable preliminary step for physical measurements upon which practical mathematics must always be based. From such physical measurements the established principles of mechanical engineering can suggest corrective measures.

This paper suggests the practice of the use of models for rubber product design on which photoelastic effects can be produced to show the location of stress distribution. By having such an actual picture of his problem, the engineer can safely select, distribute, and profile his materials on a model scale. Quantitative application of this method provides a means for determining actual service stresses. These can be related to material ultimate strength for the purpose of approaching the stress-minima criterion of maximum dynamic life. This eliminates uncertainty, speed design, reduces experimental material losses, and minimizes much expensive product testing.

OTHER METHODS OF STRESS ANALYSIS

Photoelastic analysis is simply one of several methods that the mechanical engineer has employed in the problem of determining the magnitude and direction of principal stresses in products and structures of rigid materials.

Stress-coat.—For this same objective stress-coat technique may be used. This is based on the use of lacquers which crack at predictable elongations when carefully applied under very exacting conditions. By selecting a range of such lacquers, one observes the amount of strain on the surface to which the lacquer was applied. From the amount of strain indicated by cracking of a particular lacquer and the application of variations of Hooke's Law, the actual direction and magnitude of stress on a product surface can be computed.

Strain gauges.—The use of strain gauges has become widespread. This is based on the principle that certain metals have a known electrical resistance which changes with state of strain. Strips of such metal, adhered to surfaces under measurement, reveal the degree of strain on the surface to which they are attached. Again, from such measurements the engineer can compute the direction and magnitude of stresses on the surface of interest.

Grid or photogrid techniques.—In principle, grid technique consists of laying out grids on the surface to be studied. The linear and the angular displacement of these grids of predetermined dimensions are observed. A graphical or analytical solution is then possible. This translates the known stress-strain relations of the subject material into the direction and magnitude of the principal stresses on its surface under the conditions tested. The method of Mohr's circles of strain and stress may be applied. The method of stress-strain circles is basically a procedure which can be applied to any problem of stress analysis where strain measurements can be made. It is applicable with strain gauges as well as with the grid technique.

In rubber product design, because of the large strains encountered and because of the complicated nature of the stress-strain relation, these methods apparently have not found favor.

ELEMENTS OF THE PHOTOELASTIC EFFECT

PRINCIPLES AND THE APPARATUS EMPLOYED

Certain chemical substances, by virtue of their molecular structure or of their state of subdivision, have the capacity for polarizing light. Such materials, when laminated between suitable glass disks, form a polaroid plate which allows the transmission of light vibrating in but one plane. An additional optical principle is of importance in this technique. This is the fact that transparent or translucent materials are generally birefringent to some degree when under stress. That is to say, they develop two different indices of refraction under stress. Assume a model to be studied is made of such material, and a polarized beam of light from a polaroid plate (the polarizer) falls upon this model. It will be refracted at two different angles, depending on the magnitude of the stress. On emerging from the model, these refracted beams of light either interfere with or reinforce each other. This action forms dark and light bands, or colored bands, which can be related to the stress concentrations in the model. To observe these effects on light waves after they have passed through the model, it is customary to view the model through a second polaroid plate. This plate (the analyzer) is on the opposite side of the model from the polarizer.

The apparatus actually used is shown in Figures 1, 2, and 3. To produce certain stresses on model sections, jigs were prepared for each type of loading. Mechanical lever systems, air pressure, hydrostatic pressure, and spring loading were used in this work. A sodium light source was used when a monochromatic source was desired.

INTERPRETATION OF PHOTOELASTIC LINES

The condition of stress at a given point in a model can be determined by the magnitude and direction of two principal stresses. The apparatus produces photoelastic lines indicating the difference in magnitude and the direction of these principal stresses.

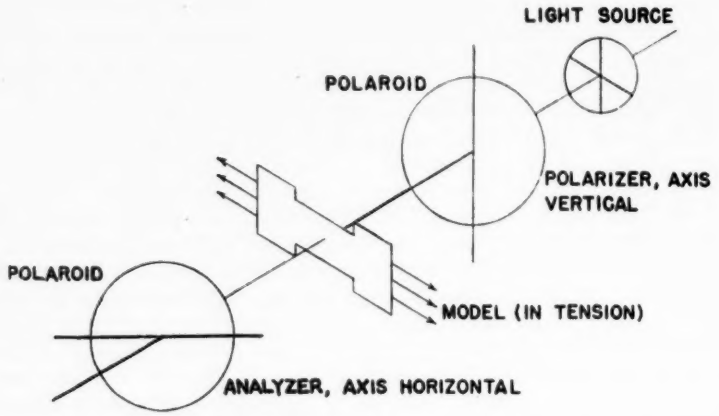

FIG. 1.—Schematic plane polariscope.

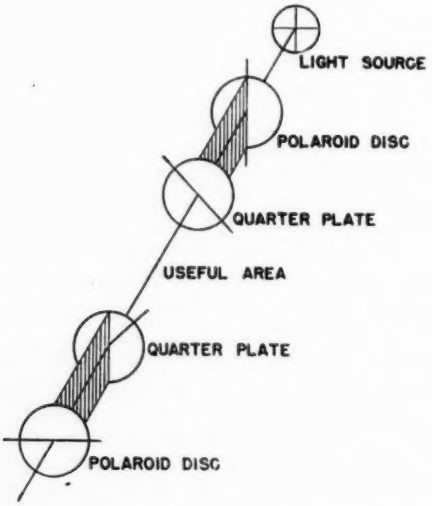

FIG. 2.—Standard polariscope.

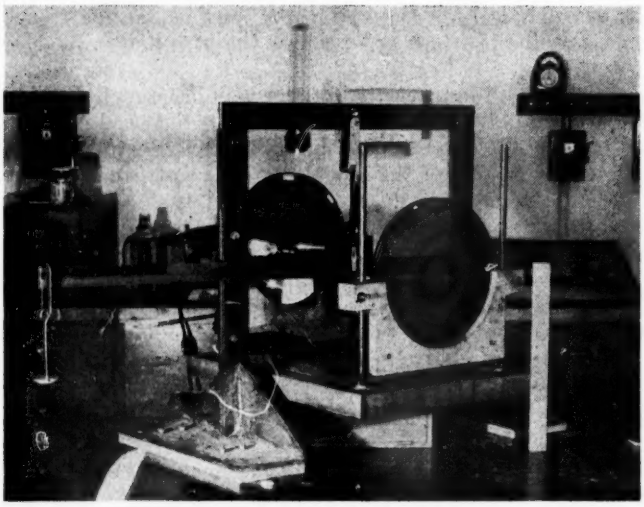

FIG. 3.—Polariscope used by the authors.

Isoclinic lines represent the inclination, or direction of principal stresses. A simple polariscope, employing polarizer, model, analyzer, and white light, shows black and colored lines on the model as viewed from the analyzer side. The black lines are isoclinic lines.

When the plane of polarization of the incident light from the polarizer coincides with the direction of one of the principal stresses, the light passes straight through the model. The analyzer plate must, therefore, be rotated so that its plane of polarization is at right angles to that of the polarizer (see Figure 1). This means that light passing straight through the model is extinguished, or cut out, when passed through the analyzer. Therefore the isoclinic lines are dark.

The direction of principal stresses are also perpendicular to planes free from shear in the model. Planes free from shear are called principal planes.

Isochromatic lines are the colored lines popularly associated with the photoelastic effect. It is often desirable to examine the model from the point of view of determining the magnitude of the difference between principal stresses rather than simply their inclination. For this purpose the isochromatic, or colored lines, are observed. To produce only isochromatics (no isoclinics present) it is necessary to use circularly polarized white light. In an ideal sense, complete circular polarization is possible only with monochromatic light. To obtain circularly polarized light, it is necessary to use a quarter-wave plate on the model side of the polarizer and analyzer (see Figure 2). These quarter-wave plates are simply additional polaroidlike disks whose light planes are rotated 45 degrees from the light plane of the polarizer or the analyzer. They are so rotated that the light planes of both quarter-wave plates are at 90 degrees to each other.

It is a principle of the photoelastic effect that, at any point on any isochromatic line, the difference between the value of the principal stresses is constant. If the model is progressively stressed, lines appear and move steadily outward from some source point or origin of stress. The order, or fringe order,

of a line is determined from the number of lines emanating from the origin. For example, the line of fringe order five is the fifth line to have appeared at the origin as loading progressed.

For a quantitative interpretation of the photoelastic effect, it is necessary to determine the actual stress concentration to produce each line by a separate calibrating test on the model material. This is accomplished in the same apparatus set-up. A strip of the model material, cut from the same sheet or plate from which the model itself was constructed, is separately loaded. With the use of appropriate jigs and loading devices the stress necessary to produce each order of line is noted on the sample tension or compression strip. For example, if a stress of 100 lbs. per sq. in. is needed to produce a line in the specimen under tension, then the difference in magnitude of the principal stresses along a fifth order line would be five times 100, or 500 lbs. per sq. in. This assumes a linear stress-strain relation holds for such a specimen.

By definition, the maximum shear stress (S_{max}) is equal to one-half the difference between the two principal stresses.

$$S_{max} = \frac{P - Q}{2} \text{ where } P \text{ and } Q \text{ are principal stresses.}$$

In the example above, substantially pure tension is the single principal stress. The maximum shear stress along a fifth order line, therefore, would be 500 divided by 2, or 250 lbs. per sq. in.

We shall defer further quantitative considerations until some typical qualitative applications have been discussed.

We shall frequently refer to fringe value. This term might be broadly considered an index of modulus. In photoelastic work it is conventionally expressed in pressure units for shear per unit thickness per band (photoelastic line, or fringe). It is, for example, the pounds per square inch per inch thickness necessary to produce two successive repetitions of a photoelastic light band.

QUALITATIVE APPLICATIONS—MATERIALS AND METHODS

FRINGE VALUE, DEFINITION AND UNITS

In classical photoelastic work, this definition has made possible one value, f, for each material at a given temperature. In the extension of this technique to rubberlike materials, the nonlinear condition again makes necessary modification of classical definition.

We must modify the term fringe value in this work to pounds per square inch shear per one-inch thickness per whatever particular fringe order or band is associated with the subject load. When fringe value is used in this sense, we will identify the fringe order involved; otherwise the classical definition will hold.

We shall discuss later the relation of material *vs.* model fringe value and the conversion of fringe value in shear to that in tension.

SELECTING SUITABLE LOW-MODULUS PHOTOELASTIC MATERIAL

Most of the work which has been done in the science of photoelasticity has employed bakelite and celluloid. Some work has also been done with gelatin. It has been used, for example, to study stresses imposed on underground structures by soil. Bentonite clay suspended in water has been used in flow

study by Leaf[1] and others. We have also utilized gelatin as a medium in a study of flow through different types of sprues. Because large strains usually must be imposed on the model, we have not found bakelite and celluloid to be suitable when a stress condition is being simulated on a rubber product. Naturally, where information is desired on stresses set up in molds or rubber manufacturing machinery, bakelite and celluloid play the same role as in the general analysis of rigid bodies by photoelastic methods.

The modulus of bakelite, and its fringe value, may be reduced by raising the temperature. This would give it some potentiality as a model material for rubber products. The technique, however, is complicated because it is then necessary to maintain a constant model temperature (about 230° F). Problems of heat control are injected into the work. Constant temperature must be maintained during the time the model is loaded and measurements and photographs are taken. It is a difficult technique, although not an impossible one. Frocht[2] reports these typical figures for the material fringe value f of BT-61-893 bakelite:

	70° F	230° F
f (lbs. per sq. in. shear stress for one-inch thickness per band)	43	1.6

The above values mean simply that at 230° F only about 1/27 the amount of stress is necessary to produce two successive photoelastic lines than is required at 70° F.

We have employed successfully substantially pure crepe rubber gum compounds as are formulated below. Their fringe values are approximately 1.7 lbs. per sq. in., tension for one-inch thickness at approximately 75° F. Expressed in terms comparable to the data of Frocht above, this value would be 1.7 divided by 2, or 0.85 lb. per sq. in. shear per one-inch thickness. The modulus values at 100 per cent elongation are approximately 100 lbs. per sq. in.

	A	*B*
Pale crepe	100	100
Sulfur	1.5	1.5
Zinc oxide	0.75	0.5
Stearic acid	0.5	
Tuads (Ethyl)	0.25	
Thionex		0.19
Acrin		0.5

TABLE 1

TYPICAL MATERIAL FRINGE VALUES f

(lbs. per sq. in. shear stress per one-inch thickness per fringe order)
Temperature range: 70–75° F

Material	Approximate plastic elastic state	Typical stress strain	
Bakelite BT-61-893 (Frocht)	Rigid plastic proportional stress/strain	No actual data reported	43
Geon-1437	Thermoplastic	800 lbs. per sq. in. 50%	4.5 fringe order 6 1.0 fringe order 1
Pure crepe rubber gum	Highly rubberlike	100 lbs. per sq. in. 100%	0.86 (roughly constant over 5 fringe orders)
Gelatin solution 13% approximate (Frocht)	Viscous fluid	No actual data reported	0.0725

Geon-1437 has been found of considerable usefulness in this technique, although subject to some creep and relaxation. We shall discuss later the effect of these phenomena. The fringe value in tension varies from 2.06 to 8.9 lbs. per sq. in. for one-inch thickness for fringe orders 1 and 6, respectively. Again, comparing this to Frocht's data above, this range in shear stress would be in the order of 1.0 to 4.5 for fringe orders 1 and 6. The modulus of the Geon-1437 used was approximately 800 lbs. per sq. in. at 50 per cent strain.

Gelatin solutions provide a still lower fringe value. Frocht[3] reports 0.0725 lb. per sq. in. shear stress for one-inch thickness at 70° F for aqueous solutions indicated to be in the order of 13 per cent.

In Table 1 we have summarized data discussed so far. This more clearly shows the relation of fringe value with the plastic-elastic state.

SIMPLE APPLICATIONS OF PHOTOELASTIC ANALYSIS

A qualitative interpretation of the photoelastic effect in a model can be obtained by simply noting the concentration of the principal stresses from a general examination of the lines, their origin, and contouring.

Milking machine inflations.—A flex-cracking problem was being encountered in a certain milking machine inflation design. Stresses in this particular design were studied by molding inflations from the clear pale-crepe gum compound. Sections were cut and stressed. Isochromatic lines were produced in the sections, using the standard polariscope and quarter-wave plates and white light. Weaknesses in the sectional design were revealed by this study. Since the inflation mold was the property of the customer, no design changes were possible. This study, however, made possible the only alternate solution to the problem—that of adjustment in the modulus of the stock. Field testing and accelerated product testing of the recompounded inflations confirmed the findings of this analysis, and the service problem was substantially eliminated.

Pressure control diaphragms.—Rubber diaphragms, as employed in some pressure control instruments, have been studied by molding them in the regular rubber product mold from clear pale-crepe gum compound and from Geon. Model diaphragms have been made with and without fabric. In obtaining satisfactory diaphragms with fabric, some difficulty was experienced in keeping the fabric from "floating", or from being displaced as a result of flow of the compound during molding.

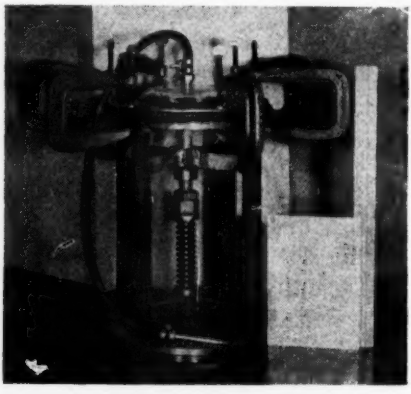

FIG. 4.—Diaphragm loading jig.

The apparatus set up as employed is shown in Figure 4. A transparent rigid plastic top with a pressure connection enables observing the photoelastic diaphragm's behavior. The apparatus could be placed in the polariscope, and any desired diaphragm displacement could be obtained and maintained. Four or five fringe orders were observed in the region of high stress, suggesting improvements in design with respect to reinforcing ribs and location of fabric reinforcement.

It should be noted, however, that diaphragms must articulate, with spring constants specified by the customer. Design changes, therefore, must satisfy not only redistribution of stresses, but also mechanical compatibility with springs used.

Mold sprue design.—Because of a molding problem it was desired to study the flow of stock through the sprue of the mold. One useful picture of the problem was made by using clear pale-crepe gum compound and Geon in loading frames (see Figures 5 and 6). Another aspect of this same problem

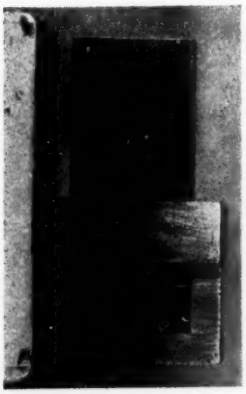

FIG. 5.—Sprue design jig.

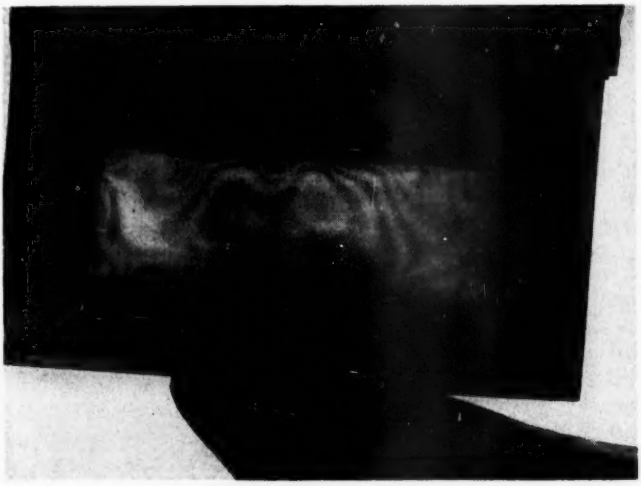

FIG. 6.—Sprue design jig—Geon sample.

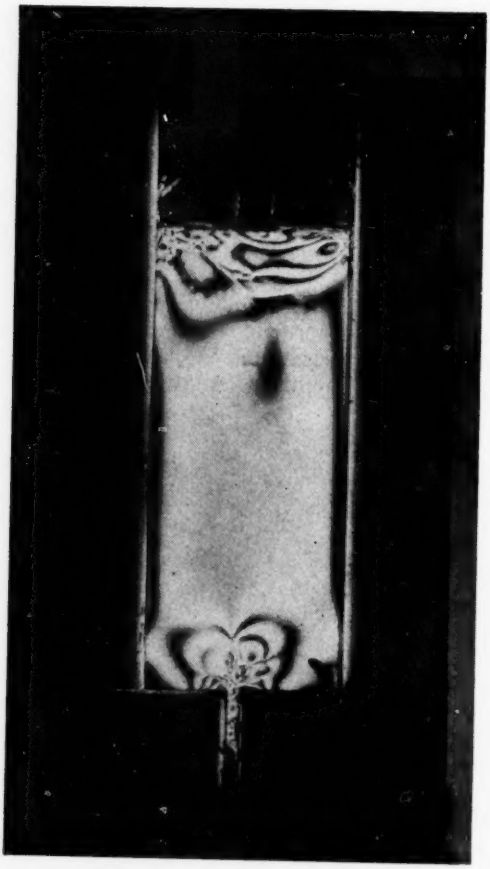

FIG. 7.—Lucite cell with gelatin.

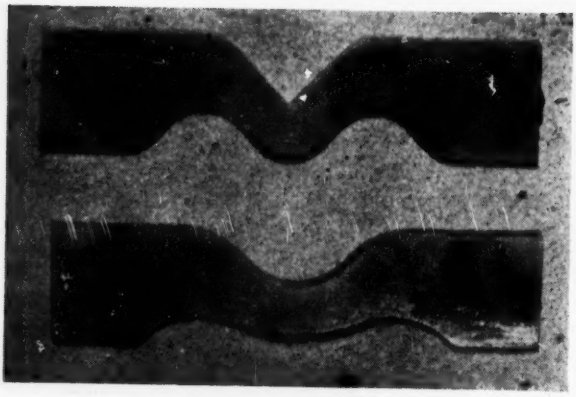

FIG. 8.—Tear test specimens—modified Graves (*Top*); Winkelmann "B" (*Bottom*).

was the behavior of plastic material around the sprue itself. This was obtained by forcing a 13 per cent aqueous solution of a good grade of gelatin through an orifice in a lucite cell and piston (see Figure 7). It can be visualized that, by modifications in this technique, processing problems in the rubber industry related to molding, extrusion, and forming can be studied.

Tear testing specimens.—In the field of rubber test-specimen design the photoelastic method was successfully used in studying stress relations in the Winkelmann B tear specimen. These stress relations were compared with a Gates modification of the Graves tear specimen (see Figures 8, 9, and 10).

In tear testing technique, using material of high distensibility, one of the main difficulties lies in concentrating shear stress in the region of tear. Another difficulty is the inability to obtain uniform nicking.

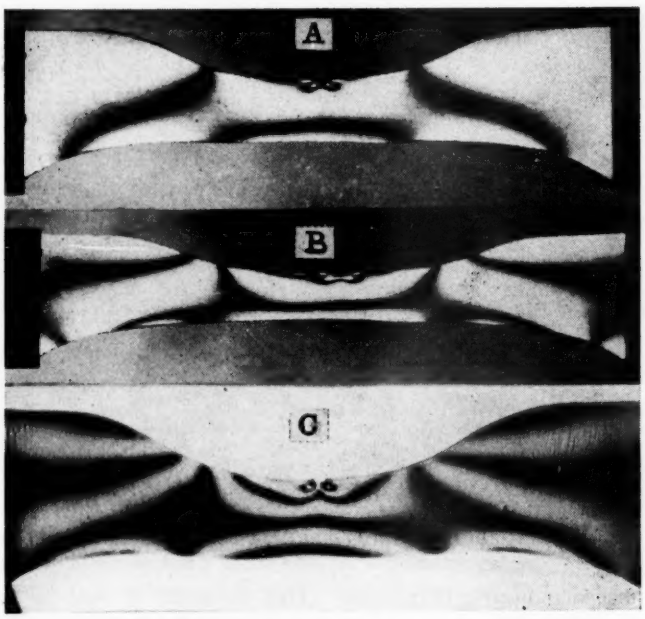

FIG. 9.—Winkelmann "B" tear model: A, light load; B, moderate load; C, severe load.

The Winkelmann B tear specimen is a nicked or cut specimen (see Figure 9). The Graves tear specimen is unnicked. The Gates modification of the Graves tear has a rounded contour opposite the region of high shear (see Figures 8 and 10).

Using the same stock, the ratio of tear values, Winkelmann to Graves, is approximately two to one, depending on gauge values and stock employed. Photoelastic analysis of this testing problem shows that a high stress concentration occurs at the right angle in the Graves tear specimen. In the Winkelmann B the stress was not highly concentrated at the nick. This condition gave evidence that in the Winkelmann tear the stress was largely tensional. This point furnishes an explanation for the two to one ratio of tear value.

There are applications in rubber technology where it is desirable to compute actual stresses existing in some part of a product under some condition of

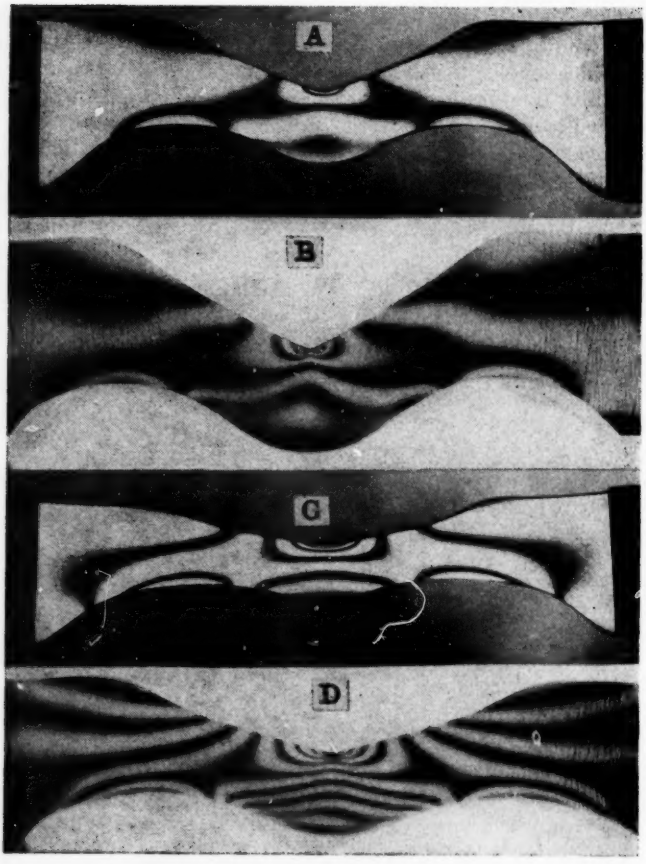

FIG. 10.—Graves tear model: A, very light load; B, light load; C, moderate load; D, severe load.

deformation encountered in service. This information may be desired to insure that the material selected has sufficient ultimate strength to withstand maximum service stresses. In certain rubber products, ultimate stresses and strains are rarely encountered. The actual stress encountered in service is of particular value in such applications to design toward the stress-minima criterion of maximum dynamic life.

QUANTITATIVE APPLICATIONS

CERTAIN LIMITATIONS IN QUANTITATIVE APPLICATION TO RUBBER PRODUCTS

In spite of definite limitations in such quantitative applications to rubber products, which we shall discuss below, photoelastic analysis does lend itself to determining actual stress value. Considerable work has been done, for example, in which bakelite beams and other structures have been stressed, and the stress which was obtained photoelastically has been checked against calculated values. In this case we can say that the photoelastic determination of

stress in a beam has an analytic counterpart in the sense that there are mathematical expressions for the calculated stress in the beam.

Lack of analytical counterpart for cases of large bending.—As we have pointed out, in rubberlike materials in service, such as hog-beater paddles, milking machine inflations, diaphragms, tires, and belts, the deformation or unit strain is relatively large. For such relatively large strains a complete analytical (mathematical) background is not usually available. This lack is a limitation in photoelastic analysis applied quantitatively to rubber products in this sense only. It denies the opportunity in many applications for checking photoelastic stress determinations against theoretical or calculated values.

Let us illustrate this principle further by a purely mathematical picture of the complication introduced by the condition of so-called large bending.

The basic expression applied to beams in small bending is an approximation:

$$M = EI\frac{d^2y}{dx^2}$$

where M = bending moment
E = modulus of elasticity
I = moment of inertia of the beam section

and $\frac{d^2y}{dx^2}$ is the curvature expression describing the beam deflection.

For large bending, as exemplified by service conditions in rubber products, the complete expression must be used. This introduces obvious complications in the analysis. This complete expression would then be:

$$M = \frac{EI\frac{d^2y}{dx^2}}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}}$$

The nonlinear relation.—Photoelastic analysis on rigid structures and using substantially rigid photoelastic materials, such as bakelite, lends itself to the use of Hooke's Law. In such cases the stresses and strains obtained show both a linear relation to each other and to the fringe value.

In rubberlike materials the stress-strain relations are not linear, nor is the fringe value linearly proportional to stress-strain. This is a limitation in the use of this method only in the sense that it is therefore necessary to determine the fringe value across the entire range of strain encountered by the product in service and therefore introduced into the model.

Lack of critical data on photoelastic materials.—The literature lacks data on photoelastic analysis applied to rubber products. There has not been published any extensive range of useful figures on photoelastic constants of rubberlike materials relating fringe value with stress-strain, modulus, Poisson's ratio, etc. We do not deal with Poisson's ratio in this paper. It is a necessary coefficient in certain mathematical methods which can be used to check the results of photoelastic analysis in particular cases. This lack of data is a limitation in the sense that the application of the method for quantitative purposes will be retarded by the necessity of collecting such information before the method can be successfully applied to a given problem.

Creep and relaxation effects.—In the work done by the authors, attempts have been made to minimize the effects of creep and relaxation. The time

required to load specimens has been reduced as much as possible to diminish these effects. We recognize that some errors exist because of these factors. It is felt that they are not serious. Creep and relaxation phenomena are limitations where particularly exacting data is required.

NECESSARY PHYSICAL CONSTANTS FOR QUANTITATIVE PHOTOELASTIC ANALYSIS

The first step in the quantitative application of the method is the determination of the photoelastic constants of the material being used. A calibrating sample of the model material is loaded throughout the entire range of strains to be encountered in the model. The fringe values associated with the stress, strain, and modulus are determined.

The calibrating sample may be one in tension, compression, or in bending. We have chosen the tensile method for this discussion because it lends itself better to explanation of the technique.

The apparatus employed for such a calibrating test[1] is as shown in Figure 3. A tensile dumbbell specimen is placed in clamps so that it may be observed between the plates of the polariscope. The lower clamp is held by a pin to a counterbalanced lever system so that the specimen can be loaded. The upper clamp is fixed. Weights may be added or removed to produce the stresses desired.

Assume a homogeneous material in a tensile specimen of uniform cross-section, XY (Figure 11). As the loading in the polariscope is increased, employing white light, a succession of colors appear in the central portion, XY. Each color brought out by the increasing load is uniform over this central portion of substantially uniform tensile stress. The sequence of colors ob-

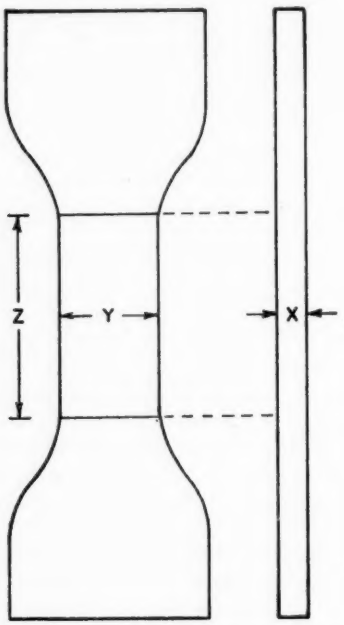

FIG. 11.—Tensile specimen of uniform cross-section.

tained is repeated as the loading continues. For calibration purposes it is sufficient to select only one color and observe the load increments causing its reappearance. If monochromatic light is used, the central portion of the specimen appears alternately light and dark as the load is increased.

From measurements of load, length, thickness, width, and their changes as the specimen is stressed, we can compute constants such as shown in Tables 2 and 3 and derived in the following manner.

For purposes of discussion, let us take our loading tests on the gum-rubber tensile specimen calibrated for preparation of Table 2:

Color sequence	Fringe order	Load (in grams)
No color	0	0
First appearance of selected color	1	165
Second appearance of selected color	2	281
Third appearance of selected color	3	379
Fourth appearance of selected color	4	463
Fifth appearance of selected color	5	527

Let us suppose the tensile specimen under discussion is shown in Figure 11. Z is the distance between bench marks: Y is the width, and X is the thickness. The change in the value of Z (or ΔZ) divided by Z is the length strain, or the strain in Z. Similarly the change in the value of Y (or ΔY) divided by Y is the width strain, or the strain in Y. The thickness strain, X, is defined in a similar manner. The cross-sectional area of the central portion of the dumbbell at any load would be the product of thickness and width (*e.g.*, XY) at the load. Similarly, volume would be the product XYZ at any load. For a substantially uncompressible material, volume should remain constant over the loading range. This provides a check on the accuracy of the linear measurements of X, Y, and Z.

If we obtain a value of load for each fringe order, then this value of load divided by the cross-sectional area (*e.g.*, XY) is the stress. If original area is used, we call the measurement *uncorrected stress*. If the actual loaded area is used, we call the measurement *corrected stress*.

Modulus is stress divided by strain. If the stress is calculated on the original area of specimen, this modulus calculation is uncorrected, since it involves uncorrected stress. If corrected stress is used to calculate modulus, then the modulus is corrected.

Table 2 shows computations for a range of fringe orders in loading and unloading of crepe rubber gum compound *A*. The material fringe values in tension (Tables 2 and 3) were obtained by taking the corrected stress at a given fringe order and multiplying by the thickness of the specimen at this fringe order.

For example, in Table 2, the corrected stress for the first fringe order is 23.8 lbs. per sq. in., the thickness is 0.072 inch.

Material fringe value in tension = 23.8 (0.072) =
1.71 lbs. per sq. in. at fringe order, one, for one-inch thickness

As explained earlier, the fringe value in shear is one-half that in tension, or 0.86 in the example given.

The average fringe value shear per band, as given in Tables 2 and 3, corresponds to the classical definition of material fringe value f. It is obtained by dividing the value in shear by the corresponding fringe order.

TABLE 2

PURE CREPE GUM COMPOUND *A*. TENSILE DUMBBELL ¼ BY 1 BY 0.075 INCH (NOMINAL); STANDARD POLARISCOPE—SODIUM LIGHT; SPECIMEN PRECYCLED 10 TIMES; TEMPERATURE 75° F

	Fringe order	Load (lbs.)	Z Length (in.)	X Thickness (in.)	Y Width (in.)	Area (sq. in.)	Stress		Modulus		Fringe value (lbs. per sq. in.)		Average fringe value (lbs. per sq. in. shear per band)
							Original area (lbs. per sq. in.)	Actual area (lbs. per sq. in.)	Original area (lbs. per sq. in.)	Actual area (lbs. per sq. in.)	Tension	Shear	
	0	0	1.04	0.0805	0.237	0.0191	uncorrected	corrected	uncorrected	corrected	...	...	...
↑Load↓	1	0.364	1.27	0.072	0.212	0.0153	19.1	23.8	86.4	107.7	1.714	0.857	0.857
	2	0.618	1.66	0.0635	0.186	0.0118	32.4	52.4	54.4	87.9	3.32	1.66	0.83
	3	0.835	2.06	0.057	0.164	0.00935	43.7	89.3	44.5	91.0	5.08	2.54	0.85
	4	1.015	2.62	0.051	0.146	0.00745	53.1	136.2	34.9	89.6	6.94	3.47	0.87
	5	1.16	3.15	0.047	0.135	0.00635	60.7	182.7	29.9	90.0	8.58	4.29	0.86
↑Unload↓	4	0.981	2.71	0.048	0.145	0.00696	51.4	140.9	31.9	87.5	6.76	3.38	0.85
	3	0.798	2.22	0.055	0.160	0.0088	41.8	90.7	37.0	80.3	4.98	2.49	0.83
	2	0.581	1.77	0.062	0.182	0.0113	30.4	51.4	43.4	73.4	3.18	1.59	0.80
	1	0.327	1.37	0.071	0.213	0.0151	17.1	21.7	53.9	68.4	1.54	0.77	0.77
	0	0	1.07	0.079	0.234	0.0185	...	...	...	...	...	...	...

TABLE 3

GEON 1437. TENSILE DUMBBELL ¼ BY 1 BY 0.075 INCH (NOMINAL); STANDARD POLARISCOPE—SODIUM LIGHT; SPECIMEN PRECYCLED 10 TIMES; TEMPERATURE 75° F

Fringe order	Load (lbs.)	Z Length (in.)	X Thickness (in.)	Y Width (in.)	Area (sq. in.)	Stress		Modulus		Fringe Value (lbs. per sq. in.)		Average fringe value (lbs. per sq. in. shear per band)
						Original area (lbs. per sq. in.)	Actual area (lbs. per sq. in.)	Original area (lbs. per sq. in.)	Actual area (lbs. per sq. in.)	Tension	Shear	
0	0	1.00	0.0715	0.251	0.0179	uncorrected	corrected	uncorrected	corrected	...	...	...
↑ Loading ↓ 1	0.5	1.08	0.07	0.243	0.017	27.9	29.4	349	368	2.06	1.03	1.03
2	2.16	1.16	0.0665	0.235	0.0156	120.7	138.5	753	866	9.20	4.60	2.30
3	4.01	1.27	0.064	0.222	0.0142	224	282	830	1044	18.04	9.02	3.01
4	5.56	1.39	0.0605	0.211	0.0128	311	434	797	1113	26.26	13.13	3.28
5	7.50	1.55	0.058	0.201	0.0117	419	641	762	1165	37.18	18.59	3.72
6	10.19	1.69	0.055	0.191	0.0105	569	970	825	1406	53.36	26.68	4.45

It will be noted that in Table 2 this value is substantially constant for the pure-crepe rubber gum compound *A*. This is because across the range of loadings employed up to fringe order 5, an approximately linear stress-strain proportion applied. The effect of nonlinear stress-strain on fringe value per band is shown better in Table 3 for Geon 1437.

With the explanations given, the reader should be able to follow the entries in Tables 2 and 3.

Now, to apply data on the photoelastic constant of a material in order to obtain the model fringe value, F, it is necessary to divide the material fringe value, f, by the thickness, t. For rubberlike photoelastic materials in models we must apply the particular fringe value associated with the fringe order at that point on the model. The thickness at that point must be used.

Expressed in equation form:

$$Ft = f$$

where F = model fringe value (in shear)
f = material fringe value (in shear)
t = thickness

With the above definitions in mind, we can easily understand the simple illustration from Frocht[4] relating fringe values in shear *versus* tension, and model *versus* material.

$2F$ = 500 lbs. per sq. in. tension or compression stress model fringe value
F = 250 lbs. per sq. in. shear stress, model
$f = Ft$ (where $t = 0.1795$ inch)
$= 250\ (0.1795)$
= 44.9 lbs. per sq. in. in shear for material for one-inch thickness

PROOF OF THE QUANTITATIVE POSSIBILITIES

We illustrate below how the methods described and the data of Tables 2 and 3 are employed to determine actual fiber stress. Examples chosen are a milking machine inflation section and a pressure diaphragm. As pointed out, however, in such practical applications, we frequently lack an analytic counterpart or independent basis for checking our results.

To prove the method we shall first employ an example correlating beam theory results with those from photoelastic analysis. It is evident that quantitative application of photoelastic analysis is both feasible and reliable to a practical degree.

Example 1: Calculation of beam stress from photoelastic analysis.—A rectangular beam of Geon-1437 was placed in pure bending. Actual measured beam data were:

Initial span	9.00 in.
Span under bending moment of 1.59 lb. in.	8.60 in.
Corrected modulus for fringe order 2, Table 3	866 lbs. per sq. in.
Beam width	0.550 in.
Beam width	0.563 in.

In the polariscope it was observed that approximately 2½ fringes were developed in tension from the neutral axis of the beam. From Table 3

Stress (actual area) second fringe order	138.5 lbs. per sq. in.
Stress (actual area) third fringe order for 2½ fringes	282 lbs. per sq. in.
Interpolated stress (actual area)	209.3 lbs. per sq. in.

Similarly, interpolated calibration tensile specimen thickness at

2½ fringe orders is equal to	0.066 in.

Therefore, actual tensile stress on outer beam fibers:

$$= \frac{(209.3)\ (0.066)}{0.550} = 25.1 \text{ lbs. per sq. in.}$$

From beam theory

Initial span—no load	9.00 in.
Span at load of 1.59 lb. in.	8.60 in.
Radius of curvature (calculated)	8.65 in.

$$\epsilon \text{ (Strain)} = \frac{\frac{\text{Thickness (depth)}}{2}}{\text{Radius of curvature}}$$

$$= \frac{\frac{0.563}{2}}{8.65}$$

$$= 0.0326\ (3.26\%)$$

$$\text{Tensile stress} = 866 \times (0.0326)$$

$$= 28.2 \text{ lbs. per sq. in.}$$

Example 2: Calculation of beam stress from photoelastic analysis.—The same beam was stressed until 5½ fringes appeared. The bending moment was 2.17 lb. in. The data for the beam were:

Initial span	9.00 in.
Span under bending moment of 2.17 lb. in.	7.26 in.
Modulus for fringe order 5, Table 3	1165 lbs. per sq. in.
Beam width	0.550 in.
Beam depth	0.563 in.

From Table 3

Stress (actual area) fifth fringe order	641 lbs. per sq. in.
Stress (actual area) sixth fringe order	970 lbs. per sq. in.
Interpolated stress (actual area) for 5½ fringe orders	806 lbs. per sq. in.

Similarly, interpolated calibration tensile specimen thickness at 5½ fringe orders .057 in.

Therefore, actual tensile stress on outer beam fibers:

$$= \frac{(806)\ (0.057)}{0.550} = 83.5 \text{ lbs. per sq. in.}$$

From beam theory

$$\epsilon \text{ (Strain)} = \frac{\frac{\text{Thickness (depth)}}{2}}{\text{Radius of curvature}}$$

$$= \frac{\frac{0.563}{2}}{4.05} = \frac{0.563}{8.10}$$

$$= 0.0695\ (6.95\%)$$

$$\text{Tensile stress} = (0.0695) \times (1165)$$

$$= 81 \text{ lbs. per sq. in.}$$

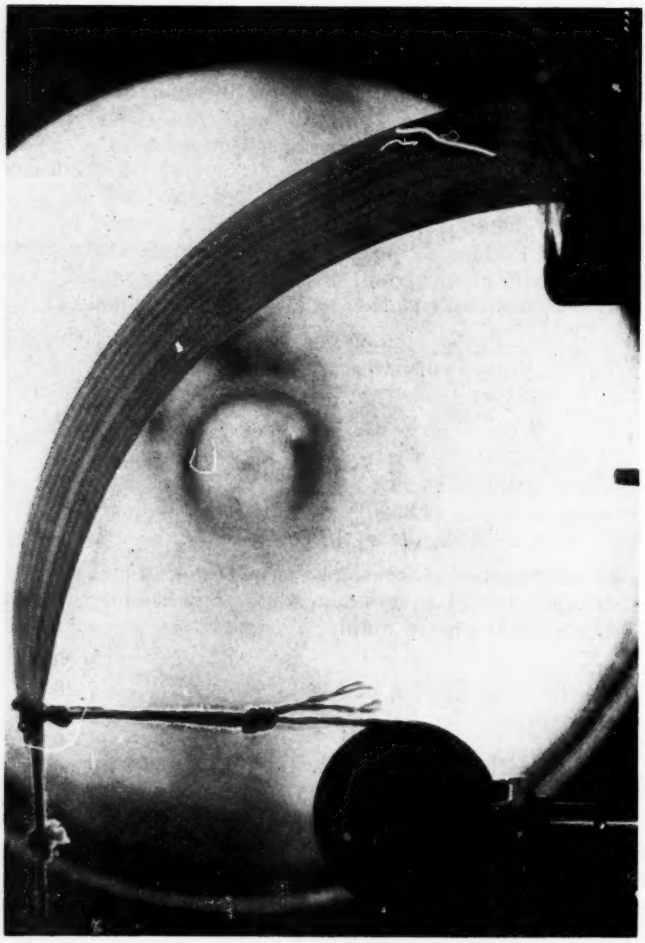

FIG. 12.—Geon cantilever uniform fiber stress.

Example 3: Uniform fiber stress in a tapered Geon-1437 cantilever beam.—In Figure 12 we have five fringes counting from the neutral axis of the beam. From Table 3 we have a corrected (actual area) stress value of 641 lbs. per sq. in. The thickness of the calibration specimen was 0.058 inch. The thickness of the Geon-1437 cantilever beam was 0.550 inch. The maximum fiber stress in tension is therefore:

$$\text{Tensile stress} = \frac{(641)\ (0.058)}{0.55}$$
$$= 67.5 \text{ lbs. per sq. in.}$$

Example 4: Milking machine inflation section.—At the high stress point in the milking machine inflation section (previously referred to) we were able to generate five bands. The section was 0.125 inch thick. Referring to

Table 2, we find corrected stress to be 182.7 lbs. per sq. in. at a thickness of 0.047 inch.

$$\text{Tensile stress in milking machine inflation section} = \frac{182.7\ (0.047)}{0.125}$$

$$= 68.6 \text{ lbs. per sq. in.}$$

Maximum shear stress = 34.3 lbs. per sq. in.

Example 5: Pressure diaphragm.—By stressing a Geon-1437 model diaphragm in the apparatus of Figure 4 to full extension of the piston, fourth order fringes were developed in the diaphragm. Selecting values from Table 3:

Corrected stress (fourth order)	434 lbs. per sq. in.
Thickness of calibration tensile specimen	0.0605 in.
Diaphragm thickness	0.203 in.

$$\text{Tensile stress in diaphragm} = \frac{(434)\ (0.0605)}{0.203} = 129.3 \text{ lbs. per sq. in.}$$

Maximum shear stress = 64.7 lbs. per sq. in.

Example 6: Frozen stress in Geon pressure diaphragm.—It may be desirable to study the resultant stresses in a complete product model under load. Stresses concurrently existing in nonadjacent or nonparallel planes under a particular loading may be of interest in a product as a whole. It can be seen that stressing cut sections does not portray the actual situation. Perhaps for a given loading condition not all sections of the complete product lend themselves to convenient photoelastic measurement, or even simple observation.

The technique of frozen stress has proved particularly valuable for this situation. The model is made of a thermoplastic material, *i.e.*, Geon-1437, and loaded at an elevated temperature such that stress relief occurs after a predetermined time. It is held at a fixed deflection corresponding to the subject load rather than at constant load.

After this stress relief period the model is cooled in the deflected position. When the model is relieved of the load deflection and returned to its normal shape, photoelastic stress lines appear frozen in the complete product. Measurements and observations may then be taken from fringes observed in various cut sections in various planes.

By such a technique in a Geon-1437 model pressure diaphragm section of 0.34 inch, we determined the tensile stress from the three fringes observed:

From Table 3

Corrected stress, three fringe orders	282 lbs. per sq. in.
Tensile calibrating specimen thickness at three fringe orders	0.064 in.

$$\text{Tensile fiber stress} = \frac{(282)\ (0.064)}{0.34} = 53.1 \text{ lbs. per sq. in.}$$

SUMMARY

Photoelastic analysis has been shown to be a feasible and reliable method for anticipating design problems in rubber products. It lends itself qualitatively and quantitatively to the selection of materials, designs, and profiles for products, test-specimens, and certain processing equipment. The apparatus, method, and calculations are relatively simple and inexpensive, as our descrip-

tion and examples have shown. It is hoped that other rubber laboratories will explore its possibilities further. More widespread use and publications dealing with this method will, we believe, contribute to a better understanding of rubber product performance and to more effective and economical use of materials.

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DETERMINATION OF TENSILE STRENGTH OF NATURAL RUBBER AND GR-S

EFFECT OF SPECIMEN SIZE *

TAKERU HIGUCHI, H. M. LEEPER, AND D. S. DAVIS

GOVERNMENT LABORATORIES, UNIVERSITY OF AKRON, AKRON, OHIO

The earliest methods used to characterize rubber involved stress-strain measurements and, although these tests have been applied more widely than any others for nearly a century, the ultimate tensile strength of rubber has seldom been studied except from purely technological considerations. The few theoretical studies of breaking strength were confined to statistical examinations of the conformity or nonconformity to the Gaussian form of the frequency distributions of the tensile strengths of natural rubber compositions[1].

The statistical distribution of the ultimate tensile strengths of GR-S has recently been studied[2]. However, there is little in the history of the science of natural rubber to compare with the rigorous treatment that has been given to the theory of breaking strengths of yarns and fibers. One of the reasons for this condition is that the performance characteristics of fibers are affected by fewer parameters than are those of rubber. Tensile strength is paramount in importance in the characterization of a fiber. On the other hand, although high tensile strengths in rubber compositions are desirable, other service properties of rubber are often of greater technical importance.

One of the phenomena associated with the tensile testing of "micro" or smaller-than-standard specimens is that the observed tensile strengths are usually higher than those obtained with specimens of the recommended size[3]. For example, Juve[4], in an examination of the effects of mill size and specimen size of the stress-strain properties found that microdumbbells (constriction dimensions, 0.125 × 0.750 × 0.075 inch) gave tensile strengths that were 20 to 50 per cent higher than those of the specification-scale specimens (constriction dimensions, 0.250 × 1.00 × 0.075 inch), although modulus and ultimate elongation values were scarcely affected by the difference in specimen size.

It seemed logical, therefore, to apply to this phenomenon a theoretical treatment similar to that given to the tensile strengths of textile fibers.

The simplest relationship suggested for fibers[5] is:

$$-dT = \alpha \frac{dl}{l} \tag{1}$$

where $-dT$ is the decrease in tensile strength brought about by an increase, dl, in length. The basis of this equation is that the relative increase in the number of weak spots is equal to dl/l. The probability of introducing a spot in the incremental segment, dl, that is weaker than the weakest spot in l, is therefore also equal to dl/l. The proportionality factor, α, may be considered as a

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measure of the heterogeneity of the fiber along its length. A similar relationship may be written for the case of rubber specimens:

$$-dT = k\frac{dV}{V} \tag{2}$$

where V and dV relate, respectively, to the volume and the increase in volume of the specimens under actual test. The volume, instead of the length, is considered in this case because, at least for a first-order approximation, the critical weak spots may be assumed to be distributed uniformly in space rather than linearly.

If the constant k is assumed to be independent of the volume, Equation 2 can be integrated:

$$-\int_{T_0}^{T} dT = \int_{V_0}^{V} k\frac{dV}{V}$$

$$\left[T\right]_{T_0}^{T} = -\left[k \ln V\right]_{V_0}^{V}$$

$$T = T_0 - k \ln \frac{V}{V_0} \tag{3}$$

A relationship such as that given in Equation 3 has been applied to the data of textile studies to estimate the degree of uniformity of fiber and yarns. A more thorough investigation of the problem of fiber strength by Peirce[6] has shown, however, that α (and therefore analogously, k) is not totally independent of the sample size. Instead of the logarithmic form, he drived the analytical relationship:

$$T_1 - T_{r1} = 3\sqrt{2}(1 - r^{-1/b})\sigma \tag{4}$$

$$\frac{T_1 - T_{r1}}{\sqrt{2}\sigma} = 3(1 - r^{-1/b}) \tag{5}$$

where $(T_1 - T_{r1})$ is the decrease in tensile strength for textile fibers brought about by an r-fold increase in sample size and σ is the standard deviation in data for the sample size represented by $r = 1$. According to experimental results, both tensile strength and standard deviation decrease steadily with an increase in sample size as shown in Table I.

TABLE I

EFFECT OF SPECIMEN SIZE ON TENSILE STRENGTH AND STANDARD DEVIATION

Relative specimen size, r	Relative decrease in tensile strength, $\frac{T_1 - T_{r1}}{\sqrt{2}\sigma}$	Relative standard deviation, $\sigma_1 = 1$
1	0	1
2	0.39	0.82
3	0.59	0.74
4	0.73	0.70
5	0.83	0.66
10	1.11	0.58
30	1.48	0.49
40	1.57	0.48
80	1.75	0.44
100	1.81	0.42

Evidence presented subsequently in this paper supports the belief that Equation 4 holds as well for rubber specimens as for textile fibers if relative volume is substituted for relative length. In the case of rubber, Equation 3 is more practical experimentally than Equation 4 in testing this relationship.

Since $r = V/V_0$ and $r^{-1/5}$ can be shown, on expansion into a series, to be approximated by $1 - \frac{\ln r}{5}$, it is evident that Equation 3:

$$T_0 - T = k \ln \frac{V}{V_0} = k \ln r$$

is analogous to Equation 4:

$$T_l - T_{rl} = 3\sqrt{2}(1 - r^{-1/5})\sigma = 3\frac{\sqrt{2}}{5}\sigma \ln r$$

if

$$k = \frac{3}{5}\sqrt{2}\,\sigma = 0.85\,\sigma \tag{6}$$

Within a limited range of size of test sample, over which the standard deviation may be assumed to be constant, substitution of Equation 6 in Equation 3 leads to:

$$T = T_0 - 0.85\,\sigma \ln \frac{V}{V_0} = T_0 - 2.303(0.85)\,\sigma \log \frac{V}{V_0} \tag{7}$$

or which experimental verification is supplied in Table V.

In the derivation of Equation 7, the frequency distribution of the tensile strength was assumed, for the sake of simplicity, to be normal; actually for natural rubber it is skewed slightly to the low side and more so for GR-S[2]. Even if normal distribution is assumed for specimens of small size, Peirce has shown that theoretically a skewed distribution is obtained for larger specimens.

In the first portion of this investigation, two stocks of GR-S and one of natural rubber were tested for tensile strength over a range of specimen sizes. The second portion of the investigation, directed to estimation of polymer heterogeneity, involved the use of a specially designed tensile strength specimen of small effective volume.

PROCEDURE

The investigation consisted of two parts.

Natural rubber and GR-S carbon black stocks.—Natural rubber smoked sheet sheet and two standard GR-S reference polymers (X-243 and X-298) were employed. Normal recipes for compounding tread stock were used and optimum cures were attained. The compounding recipes for the tread stock were:

	GR-S X-243	GR-S X-289	Smoked sheet
Polymer	100	100	100
EPC black	50	50	50
Zinc oxide	5	5	5
Mercaptobenzothiazole	1.5	1.5	1.5
Sulfur	2	2	3
BRT-7	5	5	..
Stearic acid	..	..	2
Total	163.5	163.5	161.5

A range of relatively effective specimen sizes of 1 to 12 (Table II) was attained by the use of dumbbell cutting dies of four different widths and tensile test slabs of three different thicknesses. Thickness of the specimen was estimated to the nearest 0.0001 inch with a standard rubber thickness gauge[7]. The length of each specimen was arbitrarily taken as the distance between the benchmarks; the width was measured by a method involving mass and specific gravity measurements[8]. Exact disposition of such factors as shape, breaks outside of benchmarks, and shoulder breaks was so complex that benchmarks commonly used with the given die were employed for convenience.

The data in Tables III and IV were obtained in a similar manner except that the widths of the specimens were taken as the rated widths of the various dies, 0.125, 0.25, and 0.5 inch. In the case of the natural rubber stock, this procedure leads to an error for which correction must be made. It will be noted that there is a definite downward trend in modulus values as the width of the cutting die was increased. Since there is no reason to believe that the moduli should vary over a range of specimen sizes, the observed trend must be due to errors introduced in accepting the widths of the specimens as exactly 0.125, 0.25, and 0.5 inch. The width of a die-cut tensile specimen is greater than the calipered width of the cutting die; the magnitude of the percentage error thus introduced is influenced, among other things, by the softness of the rubber and the width of the die. When soft stocks are used, the percentage difference between the width of the cut strip and the width of the die is greater with a narrow die than with a wide one. Unfortunately, data on the actual widths of the rubber specimens are not available; accordingly, corrections in the tensile strength data in Table IV have been made on the basis of the modulus data shown.

Natural rubber and Neoprene-GN gum stocks.—The compounding recipes for the gum stocks were:

	Natural rubber	Neoprene-GN
Polymer	100	100
Zinc oxide	5	5
Magnesium oxide	..	7
Sulfur	3	..
Stearic acid	1	..
Mercaptobenzothiazole	1	..
Total	110	112

A tensile specimen of relatively small effective volume was designed. This new specimen differs from the present A.S.T.M. standard in that it embodies a cylindrical concavity which is molded into the sheet or slab from which the specimen is cut. A side view is presented in Figure 1, *A*.

This specimen design avoids sudden changes of contour, so that nonuniformity of stress distribution while the sample is under strain may be held to a minimum. Through the use of this special specimen, it was found that the probable position of break could be concentrated within a very small range. The average break occurred within 0.05 inch of the center. Thickness of the samples was determined with a standard thickness gauge modified by the addition of a specially designed presser foot illustrated in Figure 1, *B*.

All calculations that involved the special specimen were based on the thickness at the low point of the concavity. The thickness at a point 0.05 inch distant from the center is less than 1 per cent greater than the thickness at the center.

There is no intention in this paper to imply that the design of the special

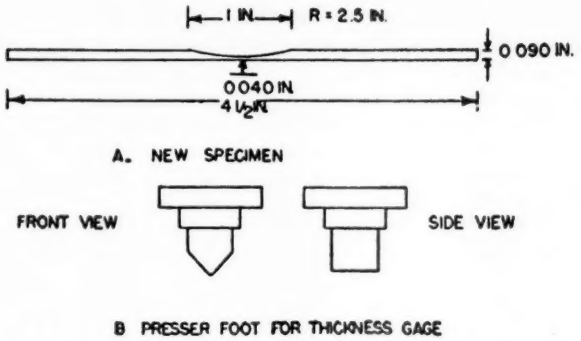

FIG. 1.—Specimen and presser foot.

test specimen is perfect. The suggestion is made simply as one attempt to devise a specimen of small volume.

RESULTS AND DISCUSSION

The results of varying the size of the test-specimen on the observed tensile strength are shown in Tables II, III, and IV and in Figure 2.

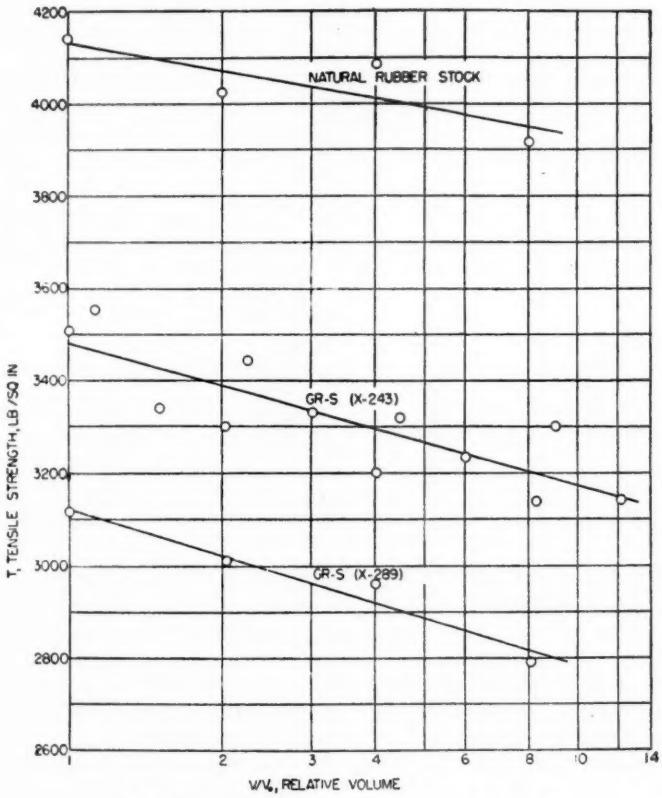

FIG. 2.—Effect of relative volume on tensile strength.

TABLE II

TENSILE STRENGTH VS. RELATIVE VOLUME OF GR-S (X-243)

Av. sample dimensions, inch	Relative volume	Modulus at 300% elongation (lbs. per sq. in.[a])	Tensile strength (lbs. per sq. in.[a])
0.125 × 1 × 0.0698	1	1350	3510
0.125 × 1 × 0.0788	1.128	1355	3555
0.125 × 1 × 0.1052	1.507	1345	3340
0.249 × 1 × 0.0710	2.025	1350	3300
0.249 × 1 × 0.0785	2.240	1400	3445
0.249 × 1 × 0.1053	3.007	1390	3330
0.248 × 2 × 0.0708	4.025	1355	3200
0.249 × 2 × 0.0786	4.484	1390	3320
0.249 × 2 × 0.1055	6.025	1375	3235
0.504 × 2 × 0.0715	8.27	1355	3140
0.504 × 2 × 0.0785	9.07	1385	3300
0.504 × 2 × 0.1053	12.17	1400	3140

Over-all standard deviation, σ, of tensile strengths = 169 lbs. per sq. in.
[a] Mean of sixteen tests.

TABLE III

EFFECT OF SPECIMEN SIZE ON TENSILE STRENGTH OF GR-S (X-289)

Av. sample dimensions, inch	Relative volume	Modulus at 300% elongation (lbs. per sq. in.[a])	Tensile strength (lbs. per sq. in.[a])
0.125 × 1 × 0.0782	1	2770	3115
0.250 × 1 × 0.0795	2.034	2775	3010
0.250 × 2 × 0.0783	4.005	2755	2960
0.500 × 2 × 0.0788	8.065	2770	2790

Average standard deviation, σ, of tensile strengths = 119 lbs. per sq. in.
[a] Mean of sixteen tests.

TABLE IV

EFFECT OF SPECIMEN SIZE ON TENSILE STRENGTH OF NATURAL RUBBER STOCK

Av. sample dimensions, inch	Relative volume	Modulus at 500% elongation (lbs. per sq. in.[a])	Observed tensile strength (lbs. per sq. in.[a])	Corrected tensile strength (lbs. per sq. in.[b])
0.125 × 1 × 0.0765	1	3835	4255	4140
0.250 × 1 × 0.0772	2.018	3730	4025	4025
0.250 × 2 × 0.0772	4.035	3700	4050	4085
0.500 × 2 × 0.0769	8.03	3650	3830	3915

Average standard deviation, σ, = 75 lbs. per sq. in.
[a] Mean of sixteen tests.
[b] Corrected to the average modulus value of 3730 lbs. per sq. in.; thus, (3730)(4255)/(3835) = 4140. Observed variation in modulus is assumed to be due to a corresponding variation in width of specimen.

A least squares treatment[9] enabled determination of constants a and b (Table V) in the equation

$$T = a + b \log \frac{V}{V_0} \tag{8}$$

and location of the curves in Figure 2.

Comparison of Equations 3 and 7 shows that $k = 0.85\,\sigma$ and comparison of Equations 3 and 8 shows that $T_0 = a$ and $k = -b/2.303$.

At least as a first approximation, the theoretical relationship developed in Equation 3 appears to be verified. A tenfold increase in volume of the test

specimen resulted in a decrease of 308 and 339 pounds per square inch in the average tensile strengths of X-243 and X-289 vulcanizates, respectively, and of 204 pounds per square inch for the natural rubber.

Practical uniformity of all modulus values in each table is evidence of the fact that all specimens, regardless of size, were vulcanized to the same state of cure.

The theoretical value of k given in Equation 6 is compared with the observed values in Table V. The agreement is satisfactory, considering the approximation used in deriving the equation and the possible error of the experimental work.

TABLE V

COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF k

	Average deviation in tensile strength (lbs. per sq. in.)	a	$-b$	k	
				Experimental $-b/2.303$	Theoretical $0.85\,\sigma$
GR-S (X-243)	169	3480	308	134	144
GR-S (X-289)	119[a]	3123	339	147	101
Natural rubber	75	4134	204	88	64
Average				123	103

[a] An unusually low value for X-289. Normal value is about 150.

It can be shown mathematically[6] that the degree of skewness is directly related to k (or, equivalently, to σ). It was shown previously[2] that the frequency distribution of tensile strength for GR-S was more skewed than that for natural rubber. This phenomenon is attributed to the higher σ and k values associated with the tensile testing of GR-S.

From the foregoing data and discussion, it is apparent that a testing procedure that employs specimens of different sizes can be adapted to evaluation of the homogeneity of cured rubber stocks. This observation is illustrated by the data of Table VI where for a normal stock and one that exhibited obvious defects, the increase in tensile strength brought about by a decrease in the effective size of the test specimen is compared.

TABLE VI

APPLICATION OF HOMOGENEITY TEST TO TWO MIXES OF GR-S (X-289)

	Observed tensile strength (lbs. per sq. in.)	
	Defective stock[a]	Normal stock
Standard size specimen	2720	3480
Special low-volume specimen	3585	3970
Difference	865	490

[a] Cured stocks of this mix exhibited pits and cones on broken surfaces.

The degree of homogeneity of cured rubber stocks can be evaluated by varying the specimen size or by determining the standard deviation for a given size. The former method requires fewer tests, is the more rapid, and would be practicable if fairly large ratios of specimen sizes could be obtained, a condition that is rather difficult to realize with the present standard testing equipment. Specimens of 4×0.5 and 0.125×0.5 inch would give an ample range; however, no stock with even a moderate elongation can be tested on the standard equipment with a strip long enough to accommodate 4 inches between bench marks.

An interesting by-product of this investigation is the application of the special specimen to the tensile testing of gum stocks of natural rubber and of Neoprene. Usually gum stocks of natural rubber and Neoprene break in the shoulder of the specimen at the point of minimum radius. The recorded values of the tensile strength of these specimens are based on the cross-sectional area of the specimen at the constricted portion. However, because of the shape of the standard specimen, the stress at the edge of the shoulder is greater than the stress at the straight, constricted portion. It has been observed that the recorded tensile strengths of Neoprene gum stocks are markedly affected by the number of nicks at the shoulder of the die. It appears then, that the rupture of gum stocks breaking at the shoulder is in the nature of a tear which starts from the surface where the stress is greatest. Carbon black stocks, though likewise suffering the greatest stress at the shoulder during the stretching operation, ordinarily break from some nuclear point of heterogeneity inside the specimen. For this reason the recorded tensile strengths of specimens that break in the shoulder are low because the stress at the breaking position is greater than the stress recorded at that instant by the tensile machine.

However, when the new form of specimen is used, the sample is forced to break near the center—the thinnest portion of the strip—because of the deliberate localization of stress at that point. This localization of stress is different from that occurring at the shoulder in one important respect—the stress at the center is easily measured, but the stress at the shoulder cannot be accurately determined. The validity of the contention is supported by the large increase in tensile strength resulting from the use of the special specimen as shown in Table VII.

TABLE VII

TENSILE TEST OF PURE GUM

	Tensile strength (lbs. per sq. in.)	
	Natural rubber	Neoprene-GN
Standard specimen	2430	4020
Special specimen	3960	5600

The differences do not, of course, involve the property of heterogeneity, but merely reflect the differences in the mechanism of rupture. It is therefore suggested that for any composition that exhibits breaks at the shoulders of standard specimens, higher and more representative tensile strength results may be obtained by using the special type of specimen.

SUMMARY

Peirce's equation, which relates observed tensile strength of textile fibers with their length, was found to be applicable to rubberlike material if specimen volume is used in place of specimen length. Experiments in which the tensile strengths of GR-S and natural rubber compositions were determined for a range of specimen volumes yielded results in close accord with theory. A tenfold increase in the volume of the material resulted in a decrease of 308 and 339 and of 204 pounds per square inch in the observed tensile strength of GR-S and comparable natural rubber stocks, respectively. The numerical magnitudes of the slopes of the straight lines obtained when tensile strengths were plotted against the logarithms of the relative specimen volumes are shown to bear direct relationships to the homogeneity of the stocks under test. The use of a dumbbell sample with a constricted center should result in a relatively

simple means of measuring quantitatively the degree of homogeneity of rubber compositions.

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THE DETERMINATION OF NITROGEN IN CRUDE RUBBER *

G. J. VAN DER BIE

NEDERLANDISCH-INDISCH INSTITUUT VOOR RUBBERONDERZOEK, BUITENZORG, JAVA

INTRODUCTION

In connection with research on the preparation of rubber with a low protein content, a method was tried out in 1938 for the determination of small percentages of nitrogen in crude rubber.

In the following year, the question was raised by Stevens[1] whether the Kjeldahl method was reliable, for with the Dumas method he had found higher values; however, this phenomenon[2] was finally found to be caused by impurities of methane in the nitrogen gas (which can be prevented by the use of lead chromate). Belgrave and Bishop's results[3] agree with these[4]. Alquier and Sirot[5] found the same results by the Dumas and Kjeldahl methods in the analysis of agricultural products.

The question raised by Stevens induced the present author to compare the figures obtained by analyses of a certain sample of rubber by means of various modifications of the Kjeldahl method with the hydrogenation method of Ter Meulen[6]. This method was applied to several samples of whole-latex rubber by Van Dillen[7], who found values 13–16 per cent higher than by the Kjeldahl method. However, it was not stated which modification of Kjeldahl was applied. Dumas determinations were not included in our experiments.

During the experiments, stress was laid especially on the short duration of destruction in connection with reliable results. When determining the nitrogen contents of rubbers poor in proteins, the results should be accurate to fractions of a milligram, since, starting from 1 gram of rubber, at the most 6–7 mg. of nitrogen and mostly less than 2 mg. is found.

THE DETERMINATION OF NITROGEN ACCORDING TO THE KJELDAHL METHOD

The procedure[8] given by the Delft Institute for Rubber Research is as follows. Place 1 gram of finely cut sample in a digestion flask; add 1 drop of mercury (about 0.6 gram) and 30 cc. of phosphoric-sulfuric acid (1 liter concentrated sulfuric acid, 200 grams of phosphorus pentoxide). When the rubber has been entirely moistened with the acid, start heating with a small flame, and, when foaming diminishes, increase the flame gradually until the liquid boils. Continue boiling for a short time after the liquid has become colorless. After cooling, dilute with water, and transfer the contents of the digestion flask to a distillation flask. The volume of the liquid is increased to about 300 cc. with water, and the ammonia formed is at once distilled after adding 150 cc. of a solution of 1000 grams of sodium hydroxide and 20 grams of sodium sulfide in 2 liters of distilled water. A few pieces of calcined pumice are added. The distillate, which should be at least $\frac{1}{3}$ of the distilled liquid, is received in a flask with 25 cc. of standard sulfuric acid (about 0.1 *N*).

* Reprinted from *Mededeelingen van het Nederlandisch-Indisch Instituut voor Rubberonderzoek* (Buitenzorg, Java), No. 64, 8 pages, November 1948.

With the low nitrogen contents of rubber, it is necessary to carry out a blank experiment.

The percentage of protein is found by multiplying the nitrogen percentage by the factor 6.25. (Although the accuracy of this factor is doubtful, it is maintained for the time being, because various investigators have not yet come to complete agreement concerning the composition of these "proteins".)

By this procedure accurately reproducible values are obtained, but it must be mentioned that a great drawback of the method is that several hours' destruction of the rubber is required. Recently selenium has been used at Delft as a destructing catalyst.

Wieninger[9] used a mixture of sodium sulfate, copper sulfate, and selenium (500 + 8 + 8 grams, respectively, and of this about 6 grams per determination); hence the sodium hydroxide need not contain any sulfide before distillation (the sulfide is necessary to decompose any mercury-ammoniacal compounds present).

Many investigators have used selenium, either as a sole catalyst or in combination with mercury or copper compounds[10].

Milbauer[11] described the advantages of 4 parts of mercury per 1 part of selenium.

For the determination of nitrogen according to Kjeldahl in fertilizers, fodder, etc., copper sulfate is generally used as a catalyst[12]. In the present research, the procedure prescribed by the Delft Institute was followed in general. After the liquid had become colorless, boiling was continued for 5–10 minutes. All chemicals, including sulfuric acid, sodium hydroxide, and sulfate were used in the pure form; therefore the blank experiment always showed less than 0.10 cc. of 0.1 *N* alkali (generally 0.05–0.06 cc.).

The copper sulfate was dehydrated by heating. For each determination, 10 cc. of 0.1 *N* sulfuric acid was used in the receiving flask.

As will be described below, a number of comparative analyses were made, using a substance with a known nitrogen content, *i.e.*, diphenylguanidine.

To approach as closely as possible the conditions of the analysis of rubber poor in proteins, such a quantity of substance was weighed for each determination as would yield 4–6 mg. of nitrogen.

As to the accuracy of the method, the following should be noted. Titrations were carried out with an ordinary burette. An error of 1 drop (0.04 cc.) 0.1 *N* titration liquid corresponds to $0.04 \times 1.4 = 0.056$ mg. nitrogen. A weighing error of 0.2 mg. in weighing the diphenylguanidine (19.9 per cent nitrogen) corresponds to 0.04 mg. of nitrogen. Hence it is impossible to expect greater accuracy than 0.06 to 0.10 mg. of nitrogen. With a microburette an accuracy of about 0.02–0.04 can be reached, at least theoretically.

ANALYSIS OF DIPHENYLGUANIDINE

The method was first applied to the standard substance, diphenylguanidine (theoretical nitrogen content 19.89 per cent), with melting point 148.5° C.

The equivalent weight at titration with 0.1 *N* sulfuric acid (indicator methyl red), theoretically 221.16, proved to be 212.

Extra organic matter in the form of sugar was added. (In the Chemischer Kalender[13] it is indicated that addition of organic matter is advisable for the destruction of substances with a high percentage of nitrogen, too low values being found otherwise.) The results of the analyses of diphenylguanidine are recorded in Table 1.

TABLE 1

Catalyst	Medium		Nitrogen (mg.)	Nitrogen found %	Nitrogen found Mg.	Theoretical error (mg.)	Average error (%)
0.75 g. $HgSO_4$	—		4.68	19.9	4.67	−0.01	−0.65
			5.23	19.4	5.10	−0.13	
0.20 g. Selenium	30 cc. phosphoric-sulfuric acid		6.38	19.4	6.22	−0.16	−2.55
			3.54	19.4	3.45	−0.09	
0.50 g. $HgSO_4$+ 0.10 g. Selenium	+0.5 g. sugar		4.24	19.8	4.22	−0.02	−0.10
			4.16	19.9	4.17	+0.01	
0.50 g. $CuSO_4$			5.97	19.7	5.91	−0.06	−1.70
			6.57	19.4	6.41	−0.16	
0.75 g. $HgSO_4$	30 cc. sulfuric acid + 10 g. potassium sulfate + 0.5 g. sugar		5.51	19.5	5.41	−0.10	−1.94
			5.33	19.5	5.22	−0.11	
0.20 g. Selenium			5.81	19.7	5.75	−0.06	−0.27
			6.27	20.0	6.30	+0.03	
0.50 g. $HgSO_4$+ 0.10 g. Selenium			5.07	19.7	5.02	−0.05	−0.25
			5.37	20.0	5.40	+0.03	
0.50 g. $CuSO_4$			3.98	19.4	3.88	−0.10	−2.97
			5.11	19.2	4.93	−0.17	
0.50 g. $CuSO_4$	phosphoric-sulfuric acid	without sugar	4.44	19.9	4.42	−0.02	−0.11
			4.40	20.0	4.41	+0.01	
0.50 g. $HgSO_4$+ 0.10 g. Selenium			5.17	19.4	5.05	−0.12	−2.65
			5.37	19.2	5.21	−0.16	
0.50 g. $CuSO_4$	sulfuric acid + sulfate		4.00	20.0	4.02	+0.02	+0.24
			4.42	20.0	4.42	—	
0.50 g. $HgSO_4$+ 0.10 g. Selenium			4.38	19.7	4.33	−0.05	−0.22
			4.78	20.0	4.81	+0.03	
0.50 g. $CuSO_4$	phosphoric-sulfuric acidα	with sugar	5.97	19.4	5.82	−0.15	−2.55
			6.57	19.4	6.40	−0.17	
0.50 g. $HgSO_4$+ 0.10 g. Selenium			4.24	19.8	4.21	−0.03	−0.48
			4.16	19.9	4.15	−0.01	
0.50 g. $CuSO_4$	sulfuric acid + sulfate		3.98	20.0	4.01	+0.03	−0.33
			5.11	19.7	5.05	−0.06	
0.50 g. $HgSO_4$+ 0.10 g. Selenium			5.07	19.7	5.02	−0.05	−0.10
			5.34	20.0	5.40	+0.06	

During the experiments it was observed that the flasks containing sulfate-sulfuric acid kept boiling more steadily than those containing phosphoric-sulfuric acid and that destruction was complete sooner.

The selenium mixture attained was destroyed more rapidly than the mixtures containing mercury sulfate.

The tables show that, when a large amount of organic substance is present, the most favorable results are obtained with the mixture of mercuric sulfate and selenium.

ANALYSIS OF RUBBER

In Table 2 the results are recorded of analyses of a rubber (A4438) with a low protein content and of a whole-latex rubber (A5407).

It is evident from these values that the nitrogen values are not greatly influenced by the use of various catalysts; only with copper sulfate were slightly lower values obtained.

The time required for destruction is decreased considerably by the use of selenium, as the liquid grows clear in a shorter time.

TABLE 2

Catalyst	Medium	Duration of digestion (min.)	Nitrogen (mg. per g. rubber)	Nitrogen (%)
Sample A4438, low-protein rubber				
0.60 g. mercury	phosphoric-sulfuric acid	120	2.23–2.24	0.22
0.50 g. $CuSO_4$	phosphoric-sulfuric acid	90	2.21–2.23	0.22
0.75 g. $HgSO_4$	phosphoric-sulfuric acid	90	2.30–2.38	0.23
0.20 g. selenium	phosphoric-sulfuric acid	60	2.27–2.33	0.23
0.50 g. $HgSO_4$ + 0.10 g. selenium	phosphoric-sulfuric acid	60	2.31–2.37	0.23
0.50 g. $CuSO_4$	sulfate-sulfuric acid	90	2.11–2.19	0.22
0.75 g. $HgSO_4$	sulfate-sulfuric acid	90	2.20–2.41	0.23
0.20 g. selenium	sulfate-sulfuric acid	60	2.18–2.24	0.22
0.50 g. $HgSO_4$ + 0.10 g. selenium	sulfate-sulfuric acid	45	2.22–2.33	0.23
Sample A5410, whole-latex rubber				
0.75 g. $HgSO_4$	phosphoric-sulfuric acid	90	6.4–6.5	0.65
0.50 g. $HgSO_4$ + 0.10 g. selenium	phosphoric-sulfuric acid	30	6.4–6.4	0.64
0.30 g. $CuSO_4$	phosphoric-sulfuric acid	90	6.3–6.3	0.63
0.30 g. $CuSO_4$ + 0.10 g. selenium	phosphoric-sulfuric acid	30	6.2–6.3	0.63
0.75 g. $HgSO_4$	sulfate-sulfuric acid	60	6.5–6.5	0.65
0.50 g. $HgSO_4$ + 0.10 g. selenium	sulfate-sulfuric acid	45	6.5–6.5	0.65
0.30 g. $CuSO_4$	sulfate-sulfuric acid	60	6.2–6.2	0.62
0.30 g. $CuSO_4$ + 0.10 g. selenium	sulfate-sulfuric acid	30	6.2–6.2	0.62
10 g. Wieninger mixture	sulfuric acid	30	6.3–6.4	0.64

The following procedure, based on the above mentioned results, is used at present by us.

Place 1 gram of finely cut sample in a 500-cc. digestion flask; add 10 grams of a mixture of 9.4 grams pure K_2SO_4, 0.5 gram $HgSO_4$, and 0.1 gram selenium (this mixture is kept in stock) and 30 cc. sulfuric acid (density 1.84). When the rubber has been entirely soaked by the sulfuric acid, start heating with a

small flame for 5 minutes, then increase the flame gradually until the liquid boils. Continue boiling for 10 minutes after the liquid has become yellow. After cooling, dilute with distilled water to 2–300 cc. Add a few pieces of calcined pumice and 150 cc. of alkali sulfide solution[14], and distill the ammonia formed[15]. Collect distillate, which should be at least 150 cc., in a flask containing 10 cc. of 0.1 *N* sulfuric acid. After distillation the excess acid is titrated back with 0.1 *N* alkali (methyl red indicator).

It is always necessary to carry out a new blank experiment when new chemicals or solutions are used. The blank should not exceed 0.10 cc. of 0.1 *N*.

DETERMINATION OF NITROGEN ACCORDING TO TER MEULEN

This method[6] is based on hydrogenation of the organic substances, *i.e.*, on the decomposition by heat in hydrogen at 300–350° C, with finely pulverized nickel as catalyst. The decomposition products are volatile hydrocarbons; the nitrogen is changed into ammonia, which is determined volumetrically. The main difficulty in this method is the mixing of the rubber with the catalyst; by the method of Van Dillen[7] the latex is mixed intimately with nickel powder and the mixture dried. In our experiments fine rubber powder (called Pulvatex[16]), which can be mixed very easily with nickel powder, was used. For lack of a nickel container, a container made of copper foil was used for heating the substance. The results of the experiments[17] are compiled in Table 3.

TABLE 3

Method	Percentage of nitrogen found	Average
Sulfate-sulfuric acid + mercury + selenium	0.311–0.297–0.297–0.300	0.30%
Wieninger	0.303–0.291–0.300–0.300	0.30%
Phosphoric-sulfuric acid + mercury	0.297–0.297–0.292–0.297–0.294	0.30%
Ter Meulen	0.297–0.292–0.295–0.297–0.295–0.292–0.298	0.30%

As the figures for nitrogen found by the hydrogenation method agree with the values found with various modifications of Kjeldahl's method, it may be concluded that these methods are reliable.

SUMMARY

It was proved that various modifications of the Kjeldahl method for determining the nitrogen content of raw rubber (with phosphoric-sulfuric acid, sulfate-sulfuric acid, mercury, copper, selenium) do not yield greatly differing values. The use of selenium as catalyst is to be preferred, since the time of destruction is shortened considerably.

A standard procedure was established.

The hydrogenation method of Ter Meulen was applied to a sample of rubber powder (Pulvatex). Since this determination gave the same results as the various modifications of the Kjeldahl method, it is concluded that all these methods are reliable.

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[15] *Chem. Kalender* **2**, 405 (1936).
[16] 1000 grams of pure sodium hydroxide and 20 grams of sodium sulfide in 2 liters of distilled water.
[17] The rubber stoppers of the apparatus should be kept in boiling 5 per cent aqueous alkali for one hour before use.
[18] *India Rubber World* **101**, No. 4, 65 (1940).
[19] The analyses were carried out by T. B. Oey.

A STUDY OF ELECTROSTATIC CHARGES PRODUCED DURING MASTICATION OF RUBBER AND OF GR-S

R. S. HAVENHILL, L. E. CARLSON, AND J. J. RANKIN

ST. JOSEPH LEAD COMPANY OF PENNSYLVANIA, MONACA, PA.

An original contribution representing "A Study of electrostatic charges produced during mastication of rubber and of GR-S", by R. S. Havenhill, L. E. Carlson, and J. J. Rankin, was published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 22, No. 2, pages 477–493, April 1949.

The authors have called attention to a number of errors, which should be corrected as follows:

Page 477—last sentence.
The word *produces* should read *produce*.

Page 479—last paragraph, 4 lines from the bottom.
The expression 3000-cycle should read 300-cycle.

Page 483—Table 2, top right heading.
The temperature 212°F should read 212° F.

Page 483—Table 2, third column of tabulated data.
The value 20.1 should read 29.1.

Page 483—Table 3, title of table.
The word POTENTIAL[6] with reference should read POTENTIAL[2].

Page 483—Table 3, heading of a second column of tabulated data.
The temperature 212°F should read 212° F.

Page 488—line 10.
The name Williams[12] with reference should read Williams[5].

Page 489—legend for Figure 13.
Temperature 41°F should read 41° F.

Page 492—table of CONSTANTS FOR AUDIO AMPLIFIER, data on transformers.
The word Putput should read Output.

Page 492—table of CONSTANTS FOR AUDIO AMPLIFIER, data on Resistors.
R_{12} and 24K should be aligned like the other items.

THE FORMATION AND STRUCTURE OF VULCANIZATES

J. BARDWELL AND C. A. WINKLER

McGILL UNIVERSITY, MONTREAL, CANADA

A paper on "The Formation and Structure of Vulcanizates" was published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 22, No. 1, pages 96–104, January 1949.

The author has called attention to an error which is present in the paper as originally published in the *India Rubber World* and which is repeated in the reprinted version in RUBBER CHEMISTRY AND TECHNOLOGY.

The error in RUBBER CHEMISTRY AND TECHNOLOGY occurs on page 97, line 17, where the expression: $\rho(2/\overline{y}_n)$, should be $\rho - (2/\overline{y}_n)$.

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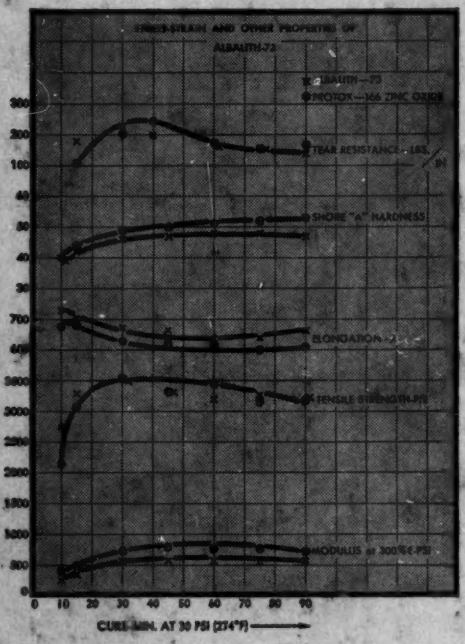

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